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MEMORANDUM

TO: LEH-11; ZEH-5: In Situ Remediation Program Sponsors

FROM: Andrew S. Green, Ph.D.
Manager, Environmental Toxicology

DATE: 11-06-02

SUBJECT: Final Report

Attached you will find the Final Report entitled "Critical Review of *in situ* Remediation Technologies for Lead, Zinc, and Cadmium in Soil" for your review and use. This report was generated by Mike Ruby *et al* of Exponent for the LEH-11/ZEH-5 Research Program.

The goal of this report was to assess the state-of-the-science with regards to existing *in situ* remediation methods for lead, zinc, and cadmium in soils. Over 400 documents were initially identified for review from which a subset of 100 were critically assessed for use in this report. The information from this review is generally presented with an overview of the different remediation strategies currently existing (e.g. in situ chemical treatments, removal, etc...), a summary of the relevant literature found for each of these strategies, and a summary of the advantages and disadvantages for each approach. Case studies are also provided when possible for each of the treatment types proving information on where the treatment was used, the type of contamination being addressed, site information, outcome of treatment, and treatment cost. Finally, this information is summarized nicely in a table (Table 11) with information on development status, regulatory acceptance, and cost for the different *in situ* treatment technologies.

Although this task has taken a long time for completion due to issues discussed with you previously (e.g. change in contractor personnel), I believe the end result is a document that provides an excellent overview and in-depth information on *in situ* remediation technologies existing today. This should prove to be a valuable resource for you and your company. Please note this report is being modified now for publication in the peer-reviewed literature.

Please contact me if you have any questions about this Final Report.

Critical Review of *in situ* Remediation Technologies for Lead, Zinc, and Cadmium in Soil

Critical Review of *in situ* Remediation Technologies for Lead, Zinc, and Cadmium in Soil

Prepared for

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Doc. no. 8601295.001 0F01 0602 R683

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Acronyms and Abbreviations

AVS	acid-volatile sulfide metals
CEC	cation exchange capacity
DoD	Department of Defense
EPA	U.S. Environmental Protection Agency
ER	electrokinetic remediation
FRTR	Federal Remediation Technologies Roundtable
GE	General Electric Company
GWRTAC	Groundwater Remediation Technologies Analysis Center
HFO	hydrous ferric oxide
HMO	hydrous manganese oxide
ILZRO	International Lead Zinc Research Organization
IRM	Iron-Rich^{TM} material
ISV	*in situ* vitrification
NTIS	National Technical Information Service
PBET	physiologically based extraction test
PCB	polychlorinated biphenyl
RTDF	Remediation Technologies Development Forum
S/S	solidification/stabilization
SEM	simultaneously extracted metals
SITE	Superfund Innovative Technologies Evaluation
SPLP	synthetic precipitation leaching procedure
SVOC	semivolatile organic compound
TBS	Thomas basic slags
TCLP	toxicity characteristic leaching procedure
TSP	Triple Super Phosphate®
VOC	volatile organic compound

1 Introduction

1.1 Purpose

To assess the extent of scientific knowledge regarding *in situ* remediation technologies for lead, zinc, and cadmium in soils, the International Lead Zinc Research Organization (ILZRO) retained Exponent to conduct a critical review and evaluation of this issue. To this end, Exponent conducted a comprehensive literature and information search to identify the most promising *in situ* remedial technologies for these metals in soil. This document presents a summary of the literature gathered during this search and provides the framework for a publishable manuscript, which will:

- Comprehensively review current and historical research on the topic

- Critically analyze and evaluate the research results in terms of success criteria

- Identify the advantages and limitations of the various remedial strategies

- Identify current research, and outstanding data gaps

- Provide recommendations for pre-remediation data collection and post-remediation monitoring.

A comprehensive search of technical and regulatory agency databases was conducted, resulting in the identification of approximately 400 potentially relevant documents. These documents were compiled in a Microsoft Excel®-based database (Appendix A to this literature review), and were given a preliminary review to identify the most relevant ones for the literature review. The resulting subset comprised approximately 100 documents, which were given a thorough review. General information regarding each study (e.g., soil type studied, scale of study [bench-, field-, or full-scale], metals concentrations, relative success, and major findings/conclusions) was incorporated into the database. The following literature review presents a synthesis of the information contained in these documents.

1.2 Overview of the Problem

The contamination of soils with toxic metals is an unfortunate by-product of the industrial age. Primary sources of lead, zinc, and cadmium contamination in soils are the mining and smelting of ores containing these metals, and the distribution of consumer products that contain these metals (e.g., lead in gasoline, paint, pesticides, and bullets). Aerial deposition of smelter emissions has led to widespread contamination of surface soils at various locations throughout the world. In addition, mining-based wastes, such as tailings, represent potential sources of metals that can be re-distributed to the surrounding environment due to aerial and fluvial

transport. Other industrial sources, such as refineries, foundries, and paint and battery manufacturers, can also be significant sources of these metal contaminants to soils.

Lead, zinc, and cadmium in soils are of concern when they are present at sufficient concentrations to adversely affect human health and the environment. In some cases, soils are so contaminated that they no longer support a functioning ecosystem. Lead is of specific concern due to its relative abundance at contaminated sites and its known potential to cause adverse health effects in children. As a result, much of the research in evaluating lead contamination has focused on reducing the exposure of humans to lead in soils. Zinc is primarily an ecological risk, because it is known to adversely affect aquatic receptors and can be phytotoxic at high concentration. Cadmium in soil represents a direct-contact risk to both human and ecological receptors due to its relatively high toxicity and plant uptake.

Given the widespread distribution of lead, zinc, and cadmium in soil due to anthropogenic activities, and the potential for human and ecological risks from these metals, it is desirable to have cost-effective remediation strategies for these contaminated soils.

1.3   Remediation Strategies for Metals-Contaminated Soils

There are relatively few fully developed, *in situ* methods available for remediation of metals in soils, and often, remediation at a given site consists of traditional remediation alternatives such as excavation (for treatment/disposal) or containment. Excavation of metal-contaminated soils is often impracticable due to the excessive cost involved, the magnitude (area, depth, volume) of the soil contamination, and the degree of disruption incurred at the site. Containment alternatives, such as soil caps are often inconsistent with the desired end use for the site, and may be viewed negatively by the regulatory community and the public.[1] As a result, there is considerable interest in identifying low-cost, *in situ* alternatives for remediation of metals-contaminated soils.

In situ remediation technologies for metals-contaminated soils center around three general strategies:

- *Contaminant Removal*—technologies that remove the metal contaminants from the soil matrix for aboveground treatment, recovery, and/or reuse

- *Contaminant Isolation*—technologies that isolate the metal contaminants from the surrounding environment through encapsulation and/or reduced permeability of the soil matrix

- *Contaminant Stabilization*—technologies that alter the geochemical state of the metal contaminants so that they are rendered less leachable, mobile, and/or bioavailable.

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[1] Physical containment strategies (such as soil caps), although technically *in situ* technologies, were not considered in this report because they do not involve treatment of the soils.

Selection of a given remediation strategy is influenced by a number of factors, including site-specific conditions, remediation objectives, desired end use for the site, and regulatory considerations. These factors are discussed briefly below.

- *Site Conditions*—Selection of an *in situ* remediation technology strongly depends on the specific conditions present at the site. The soil properties (e.g., clays vs. sands) and nature of contamination (concentration, number of contaminants, chemical form of the contaminant) can influence remedy selection. Some strategies are most appropriate for surface contamination, while others are more effective for treating metals at depth. Finally, the volume and area of contamination substantially influence the remedial strategy, because many strategies are impracticable for widespread contamination.

- *Remediation Objectives*—The desired end point(s) of the remediation will influence the appropriateness of an *in situ* remedial strategy. For example, an isolation technology may be most effective if the primary goal is to prevent leaching of the metals to groundwater, whereas a stabilization technology may be more appropriate if the objective is to reduce risk associated with human or ecological exposure to the soil. The remediation target will vary from site to site and is closely tied to the receptors considered to be at risk and the desired end use for the site.

- *Site End Use*—The desired end use for the site strongly influences remedy selection. Many remedial strategies can compromise the number of potential uses for the site following remediation. Furthermore, the site end use can influence the level of cleanup required. For example, cleanup levels are likely to be more stringent for residential uses than recreational uses, because residential uses offer greater opportunity for exposure to residual contamination.

- *Regulatory Considerations*—Selection of a remedial strategy is substantially influenced by the regulatory and community climate. Environmental regulations often set concentration-based standards, which mandate the type and extent of remediation required. Furthermore, the regulatory environment can vary from site to site, with some agencies being more amenable to innovative strategies, while others tend to support more conventional approaches. Regulatory acceptance is of particular concern for remedial strategies that rely on reducing the bioavailability of the metal in the soil. Additional research will be required before such strategies (and their measures of success; see Section 1.4.3) are universally accepted by the regulatory community.

Each of the above factors must be weighed in the evaluation of potential alternatives for remediation of metal-contaminated soils at a given site.

1.4 Measures of Successful Remediation

It is important that the measures of a successful remediation be clearly defined, and that appropriate testing procedures be used to ensure that the objectives of the remedy are achieved. In general, there are three types of primary objectives for *in situ* remediation of metal-contaminated soils:

- *Reduce metal leaching*—At many sites, there is a potential for metals to be leached from soils by infiltrating water, spreading the contamination and potentially affecting groundwater and downgradient resources.

- *Reduce metal bioavailability*—The metals in contaminated soils are often present in chemical forms that are readily bioavailable to human and/or ecological receptors. As a result, increasing interest (particularly for lead-contaminated soils) has been placed on *in situ* remedial strategies that render the metals less bioavailable, such that the metal-contaminated soil no longer represents an unacceptable risk to human health or ecological receptors.

- *Re-establish vegetative cover*—Metal-contaminated soils can be phytotoxic and are thus depleted or devoid of vegetative cover. As a result, they are subject to wind and water erosion. Thus, a common remediation strategy is to re-establish a vegetative cover on the soils to prevent further erosion and establish a healthy ecosystem that supports the local ecology.

There are no set guidelines for quantifying the success of a remediation strategy at achieving any or all of the above objectives. As a result, laboratory and field applications of *in situ* remediation technologies have often been subjected to a wide variety of measures of success, which complicates a comparative analysis of technologies. The following discussion provides background on the types of analyses that are typically performed to evaluate the success of an *in situ* remediation strategy for metals-contaminated soil.

1.4.1 Re-establish Vegetative Cover

Some metal-contaminated soils do not support plant growth due to the phytotoxicity of the metals in the soils, and/or other plant stresses posed by the soils (e.g., low pH, high salinity). The lack of vegetative cover leaves the soils exposed to erosional processes and direct contact exposures. As a result, many *in situ* remediation strategies are designed to allow for development of a vegetative cover over the metal-containing soils, thus allowing a functional ecosystem to be re-established, and provide a barrier against direct contact. It should be noted that frequently additional remedial efforts may be required (e.g., soil amendments to reduce metal bioavailability) beyond simple revegetation, to ensure that the overall remedy for the soils is protective of human health and the environment.

The effectiveness of a remediation strategy for revegetation of metals-contaminated soils is evaluated, both on the bench and field scale, through the quantitative assessment of the viability and health of plant species grown on the treated soils. This assessment includes observations of

plant mass and rate of growth, as well as indicators of metal-related stresses. In the field, the success of revegetation efforts often relates to observations of the degree of coverage that is established. Furthermore, the health of the vegetative cover can diminish with time as active components of the remedy (e.g., soil amendments) become depleted, so it is important to evaluate the health of the vegetative cover into the future. Re-establishment of vegetation on the affected soils is the first step for developing a functional ecosystem. Measures of ecosystem health are only appropriate to field-scale applications, and typically involve quantification of diversity, health, and abundance of plant and biological species (e.g., nematoads, bacteria, worms).

One important factor to consider during revegetation of metal-contaminated soils is whether the metal is accumulated in plant tissue that may be consumed by wildlife and thus represent a pathway for ecological exposure and transport of the metal to higher trophic levels. Therefore, evaluation of revegetation efforts for metals-contaminated soils typically involves quantifying the "phytoavailable" fraction of metals in soils. This quantification can be performed at the bench or laboratory scale and can involve direct measurement of metal uptake to plant tissue. Alternatively, phytoavailability can be quantified indirectly through chemical extractions (discussed below) designed to provide a measure of the readily soluble fraction of the metal in soil that would be available for uptake by plants.

1.4.2   Reduce Metal Leaching

At many sites, there is a potential for metals to be leached from soils by infiltrating water, spreading the contamination and potentially affecting groundwater and other downgradient resources. The success of an *in situ* remedy at reducing the leachability of a metal contaminant in soils is typically evaluated through laboratory leaching tests—the most common of which are the synthetic precipitation leaching procedure (SPLP) and the toxicity characteristic leaching procedure (TCLP).

The SPLP is a procedure that is approved by the U.S. Environmental Protection Agency (EPA Method 1312) and is designed to evaluate the potential for a contaminant to be released from a soil in response to infiltrating meteoric water. The SPLP test involves leaching the soil with slightly acidic water designed to simulate acidic rainfall, and determining the amount of metal leached into solution. The TCLP is another EPA-approved leaching procedure (EPA Method 1311); however, the leaching solution is designed to simulate the fluids that may be generated in a landfill, and it is thus more acidic and includes organic acids. The TCLP is generally more aggressive than the SPLP for leaching metals from soils, because it is used to assess the suitability of a given soil or waste for disposal in a landfill. As a result, the TCLP is not directly applicable for the evaluation of *in situ* remediation technologies. However, the TCLP is frequently used to assess the performance of *in situ* remediation technologies for metals and provides a reasonable, albeit conservative, measure of the treatment success at reducing *in situ* metal mobility.

In addition to the SPLP and TCLP leaching tests, several laboratory extraction procedures are used to assess metals solubility (and thus mobility) under various conditions. The simplest of these procedures quantifies the "water-extractable" fraction of metal in the soil. This test

involves mixing a set mass of soil with a set volume of water, allowing the slurry to equilibrate, and quantifying the mass of metal in the liquid phase. This test provides an indication of the relative mass of metal that is highly mobile and readily bio-/phytoavailable. Another common laboratory procedure is sequential extraction testing, which involves sequentially extracting metals from the soil with a series of more and more aggressive leaching solutions. These tests provide an indication of the how the metal mass is present in the soil matrix, and correlations can be inferred as to the probable mechanism by which the metals are present in the soil matrix (e.g., as a specific mineral species, bound to soil organic matter or oxide phase, etc.).

1.4.3   Reduce Metal Bioavailability

A recently developed strategy for reducing the risk posed by metals-contaminated soils is to render the metals less bioavailable, thus reducing the risk posed by the soil to human and/or ecological receptors. Bioavailability of a metal in soil may be measured using *in vivo* or *in vitro* methods. *In vivo* testing involves measurement of uptake in a living organism. Typically, these tests involve dosing an appropriate animal model with the metal-contaminated soil. Collection of blood or tissue samples at specific time points allows for calculation of the amount of metal absorbed by the animal. The juvenile swine model developed by EPA for assessing the oral bioavailability of lead and arsenic from soil is an example of such a testing system. In the case of lead, it is also possible to measure the oral bioavailability of lead in soil in adult humans. This has been done for a number of soil samples by measuring stable lead isotope dilution in the blood of volunteers dosed with small amounts of test soils. *In vitro* methods, such as the physiologically based extraction test, involve laboratory chemical extractions that are designed to mimic the physiology and chemistry of the gastrointestinal tract. These tests provide data on the fraction of the metal in soil that would be dissolved during digestion, and available for adsorption.

In situ remediation strategies that center on reducing metal bioavailability will be accepted by the regulatory authorities only if they accept reduced bioavailability as evidence of reduced risk, and that reductions in bioavailability are permanent. *In vivo* measures yield data that are generally more readily accepted by the regulatory community. However, these measures are extremely time-consuming and costly to obtain. *In vitro* testing methods are slowly gaining acceptance by regulatory authorities (primarily for lead), but these methods are not universally accepted, and additional research is required to validate the *in vitro* testing methods.

2 Literature Search

A literature search was conducted to identify potentially viable *in situ* remediation techno logies for sites where lead, zinc, and/or cadmium in soil are the principal contaminants of concern. The primary mechanism for identifying applicable literature was through searches of computerized databases. Databases searched included AGRICOLA (AGRICultural OnLine Access), BIOSIS Previews®, GEOBASE, GeoRef, Life Sciences Collection, National Technical Information Service (NTIS), Pollution Abstracts, TreeCD, and the European Commission Libraries Catalog. In addition, government- and industry-sponsored resources/databases were searched, including EPA's CLU-IN, EPA's REACH IT, the Federal Remediation Technologies Roundtable (FRTR), EPA's Remediation Technologies Development Forum (RTDF), Groundwater Remediation Technologies Analysis Center (GWRTAC), and EPA's Superfund Innovative Technologies Evaluation (SITE) program. Finally, gray literature and unpublished literature was acquired from Exponent staff, clients, and professional colleagues; and from searches of the Internet.

The literature search was focused on *in situ* treatment applications to remediate soils contaminated with lead, zinc, and cadmium through isolation, removal, stabilization, and/or phytoremediation processes. Containment-based technologies (e.g., capping,) were not evaluated, and are not discussed in this literature review. Searches of electronic databases and other resources typically involved key-word searches using such words as lead, cadmium, zinc, *in situ*, soils, remediation, treatment, mitigation, stabilization, electrokinetic, soil flushing, phytoremediation, and stabilization, either alone or in combination. Documents identified by these searches were screened initially based on the document title and database abstract (if available). This initial screening process identified over 400 documents (see Appendix A) that appeared sufficiently relevant to warrant further review. All of these documents were obtained, and a more detailed screening was conducted to identify the most relevant documents pertaining to *in situ* remediation of lead, cadmium, and zinc in soils, with special emphasis on documentation of field- and/or full-scale applications. This resulted in over 100 documents that were deemed worthy of a thorough review.

These documents were reviewed carefully, and the critical data, performance indicators, and primary findings and conclusions were entered into the database (Appendix A). Each document was assigned a unique citation (identification) number and a letter identifier(s) to classify it within the four general types of remediation technologies/strategies identified—isolation, removal, stabilization, and phytoremediation.

3   Literature Review

The following literature review summarizes the findings of the literature search conducted to evaluate available and promising approaches for *in situ* remediation of soils contaminated with lead, cadmium, and/or zinc. Owing to its prevalence in contaminated soils throughout the world, the majority of the documents (and associated remediation approaches) identified during the literature search address the treatment of lead in soils. However, many of the studies/applications presented herein either addressed cadmium and/or zinc as co-contaminants, or could potentially be applied to do so. As discussed above, the remediation approach(es) presented in each document were segregated into one or more of four general remediation technology types: isolation, removal, stabilization, or phytoremediation. The following presents a discussion of each remediation technology, including a summary of the findings of current research and case studies, an overview of the advantages and limitations of the technology, and a discussion of the technology status and areas that require further research.

3.1   Isolation

For the purposes of this report, isolation technologies are considered to be well-established engineering approaches that are implemented to reduce contaminant mobility by one or more of the following means:

- Reducing the exposed surface area of the contaminant (i.e., encapsulation)

- Limiting contact of the contaminant with infiltrating meteoric water and/or groundwater by reducing the soil permeability.

- Reducing the contaminant solubility by formation of insoluble metal precipitates, sorption, or non-specific inclusion within the amendment material.

Isolation technologies (often referred to as solidification/stabilization [S/S]) are relatively well established for both inorganic and organic contaminants, and the mechanisms by which they operate are generally well understood. As a result, it is not surprising that the literature search did not reveal any articles pertaining to research efforts investigating this technology. However, as noted in the EPA report, *Recent developments for in situ treatment of metal contaminated soils* (U.S. EPA 1997), "although published data generally are limited to those developed in demonstration projects sponsored by EPA, *in situ* stabilization/solidification is likely to be effective in reducing leachable concentrations of metals to within regulatory or risk-based limits." The literature search produced several overview documents describing the technology and summarizing its applications and limitations. In addition, the literature search revealed several sites where isolation technologies have been selected and implemented as part of the final remedy.

The isolation technologies described herein take the form of two general approaches—stabilization/solidification and *in situ* vitrification—which are described individually below.

3.1.1 Solidification/Stabilization

3.1.1.1 Technology Description

Solidification/stabilization (S/S) is the most common approach used to immobilize metals in soils and wastes (Evanko and Dzombak 1997). Cement-based and pozzolan materials (e.g., fly ash) are commonly used as S/S binders for metals remediation—with the predominant immobilization mechanism for metals being precipitation of hydroxides, carbonates, and silicates (Engineering Bulletin 2000; Evanko and Dzombak 1997). In addition, the permeability and porosity of the soils is often reduced, which limits the potential exposure of the metal in the soil to infiltrating water, thus limiting the potential for leaching. Lead and cadmium are particularly amenable to S/S using cement-based binders (Engineering Bulletin 2000). Organic binders, such as bitumen, polyethylene, parafins, and waxes, can also be used to stabilize metals in soils. These binders, or thermoplastics, are heated and mixed with the soils; they then agglomerate with the soils and encapsulate the contaminant. These approaches require considerably more energy and equipment than cement-based systems, and are less frequently used for metal contaminants. An advantage offered by S/S is that it can often be applied to address soils with both inorganic and organic contaminants.

Although typically applied *ex situ*, S/S binders can be mixed with soils *in situ* through the use of conventional earthmoving equipment, vertical auger mixing, or injection grouting. The primary limitation to *in situ* application of S/S technology is the ability to achieve sufficient mixing throughout the contaminated zone. Alternative methods are a focus of current research and may offer a more effective means of achieving *in situ* mixing. *In situ* stabilization is a commercially available technology, and several vendors have developed patented augers designed to achieve maximum mixing of the S/S reagent with the soil matrix (U.S. EPA 1997).

3.1.1.2 Summary of Literature Search Results

The literature search resulted in four technology overview reports detailing S/S technology (Engineering Bulletin 2000; Evanko and Dzombak 1997; U.S. EPA 1997, 1998). In addition, brief project summaries were collected for ten sites where *in situ* S/S technologies had been implemented as the remedy for lead-, cadmium-, and/or zinc-contaminated soils (U.S. EPA 2000a; USAEC 1999).

The literature search identified ten sites with lead, cadmium, and/or zinc contamination in soil, at which *in situ* S/S had been undertaken; Table 1 summarizes the performance of *in situ* S/S at these sites. Although limited data were available from these sites, the available information suggests that *in situ* S/S was largely successful at achieving the desired remedial endpoint of reducing metal mobility. In general, the success of these field trials was based on the results of TCLP testing, and the effect of treatment on the bioavailability of the metals was not considered.

Table 1. Summary of applications of *in situ* isolation technology at ten metals-contaminated sites

Site	Metals Targeted	Initial Concentration (mg/kg)	Volume Treated (yd^3)	Post-Treatment TCLP Results[a]	Citation
Pesses Chemical Co. Fort Worth, TX	Cd, Ni	Cd: 383	12,350	Stabilized soils passed TCLP for cadmium	EPA REACH IT 3/29/00, Arens Corporation
Jacksonville Naval Air Station Jacksonville, FL	Cd, Cr, Pb, Ni, Ag	Not Available	9,000	Cd: 0.19 mg/L Pb: 0.37 mg/L	EPA REACH IT 3/29/00, Bechtel
62nd Street Dump; Tampa, FL	Cd, Pb, Cr	Pb: 15,000 Pb TCLP = 224 mg/L Cd TCLP = 20 mg/L	140,000	Pb less than 5 mg/L	EPA REACH IT 3/29/00, Heritage Environmental Services.
Geiger (C&M Oil) Rantoules, SC	Cr, Pb	Pb: 740	24,000	Most samples below treatment goals	EPA REACH IT 3/29/00, McLaren-Hart
Hastings Hastings, NE	Cd, Pb	Pb: 11,600 Cd: 556	9,500	Pb and Cd: ND – 0.32 mg/L	EPA REACH IT 3/29/00, Montgomery & Associates
Pepper Steel and Alloys, Inc. Medley, FL	Pb	Pb in leachate: 98,000 mg/L	144,000	Pb in leachate: <1,000 mg/L	EPA REACH IT 3/29/00, Qual-Tech
Northern Engraving Co. Sparta, WI	Cu, Ni, Zn, F	Not Available	3,150	All EPA toxicity performance criteria met	EPA REACH IT 3/29/00, Northern Engraving Corporation Site
Sacramento Army Depot Sacramento, CA	Pb, Cd	Not Available	Not Available	Passed all TCLP tests.	USACE 1999
GE Electrical Service Shop, Hialeah, FL	Pb, Zn, Cu, Cr	Total Metals: 80–297 mg/kg	237	Reduced total leachable metals from 320–2,650 μg/L to 120–210 μg/L.	US EPA 1989
Gurley Pit, AR	Pb	Not Available	Not Available	Project completed; performance data not available.	Engineering Bulletin 2000

[a] Because the primary objective of remediation for isolation technologies is reduced mobility, remediation performance is typically evaluated through leachability tests—most commonly the TCLP.

3.1.1.3 Summary of Technology Status and Applicability

Table 2 summarizes the advantages and disadvantages of *in situ* S/S technologies for the remediation of lead, cadmium, and/or zinc in soils. *In situ* S/S is commercially available and has been demonstrated at several sites and under the EPA's SITE program. However, despite this fact, data on the performance of *in situ* S/S are limited, and concerns remain regarding the uniformity of treatment and long-term reliability (Evanko and Dzombak 1997). It is important to note that, unlike the removal technologies described later in this report, S/S does not remove the metal contaminant from the soil matrix, and thus, the long-term potential for remobilization of the contaminant from the stabilized matrix is of concern. Furthermore, S/S technologies are almost uniformly applied to achieve the remedial endpoint of reducing metal mobility. No sites or investigations were identified in which S/S was applied to reduce the bioavailability of lead, cadmium, and/or zinc. Finally, *in situ* S/S technologies can result in a significant increase in the soil volume and dramatically alter the physical and chemical nature of the soil and, as a result, can often limit the number of potential end uses for the site.

As described in Case Study #1, a technology demonstration project at the General Electric Company (GE) electric service shop site in Hialeah, Florida, found that deep soil mixing equipment was effective at mixing stabilization reagents in soils to the target treatment depths of 14–18 ft (U.S. EPA 1989). Through the use of such vertical augering techniques, *in situ* S/S can be used to target depths as great as 150 ft. However, even at relatively shallow depths, the primary limitation to *in situ* S/S application is the inability to ensure uniform delivery of the reagents throughout the contaminated zone. Furthermore, the *in situ* application of S/S technology may be precluded at sites where large rocks, cohesive soils, oily sands, and clays are present (Evanko and Dzombak 1997). For contamination at less than 8 ft deep, excavation and *ex situ* treatment are likely to be less expensive and more reliable than *in situ* S/S (U.S. EPA 1997). For S/S treatment, the site must be prepared (e.g., grubbed) prior to application and, in the event that vertical augers are used, the site must be leveled.

Costs for *in situ* S/S project can range from as low as $20–$40 per cubic yard to as much as $100–$200 per cubic yard (U.S. EPA 1997), depending on the depth and volume of soil treated. Due to the limited number of available vendors and the need for specialized augering equipment, mobilization costs are typically high (U.S. EPA 1997). Bench-scale studies are required to determine the optimum reagents/conditions prior to implementation of *in situ* S/S at a site.

**Table 2. Summary of the advantages and disadvantages of *in situ* solidification/
stabilization for remediation of soils contaminated with lead, cadmium,
and/or zinc**

Advantages

Commercially available.

Demonstrated capability for reducing lead, cadmium, and zinc mobility; and generally accepted by the regulatory community for this purpose.

Potentially effective over a wide concentration range.

Potentially effective for mixed contamination (e.g., inorganic and organic).

Can be applied to depths as great as 150 ft.

Disadvantages

May not be cost effective for shallow contamination.

Highly site specific. Soil heterogeneities or the presence of clays and other cohesive soils may preclude use of this technology.

Uniform treatment difficult to ensure/verify due to the difficulty of mixing *in situ*.

Not demonstrated for reducing metal bioavailability.

End land use may be compromised.

Long-term effectiveness uncertain.

Case Study #1: *In situ* stabilization of PCB-, VOC-, and metals-contaminated soils at the GE electric service shop[2]

Location: Hialeah, Florida

Reference: U.S. EPA 1989

Metal Contaminant: Lead, zinc, copper, and chromium at a combined total metals concentrations of 80–297 mg/kg. PCBs (the primary contaminant) and VOCs also present.

Area/Volume of Treated Area: Two 200-ft^2 areas treated to depths of 14 and 18 ft (237 yd^3).

Soil Properties: Low-moisture-content sand. Permeability of 1.5×10^{-2} cm/s, pH of 8.1, total organic carbon (TOC) of 4,380 mg/kg, bulk density of 1.51 g/mL.

Problem Statement: A Superfund Innovative Technology Evaluation (SITE) project was undertaken at the GE site to demonstrate the effectiveness of deep soil mixing and *in situ* stabilization technologies to immobilize PCBs, VOCs, and several metals (including lead, zinc, copper, and chromium) in soils.

Action: The *in situ* stabilization project was conducted on two 20-ft × 10-ft areas to depths of 14 and 18 ft. Geo-Con, Inc.'s deep soil mixing equipment was used to mix the soils within the treatment zone while simultaneously applying the stabilization reagent—a proprietary additive, termed HWT-20.

Results: The deep soil mixing equipment performed well—suitably dispersing the HWT-20 additive into the soil. The process appeared to immobilize PCBs, although analytical detection limits hindered absolute confirmation of PCB immobilization. Total TCLP-leachable metals were reduced from 320–2,650 μg/L to 120–210 μg/L. However, the physical (geotechnical) properties of the amended soils were somewhat poorer than anticipated and they tended to crumble under laboratory test conditions.

Outcome: The *in situ* stabilization process was largely successful and was demonstrated to be effective at depth in soils. The estimated cost for the demonstration project was $150/yd^3, but costs would be lower for larger scale applications.

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[2] PCB = polychlorinated biphenyl; VOC = volatile organic compound

3.1.2   *In Situ* Vitrification

3.1.2.1   Technology Description

In situ vitrification (ISV) involves the application of electric current to melt soil at high temperatures (1,600 to 2,000 °C)—causing the soil to form a stable, glass-like matrix in which most inorganic contaminants are immobilized. Organic contaminants, if present, are typically volatilized or pyrolyzed during the treatment.

3.1.2.2   Summary of Literature Search

Applications of ISV are limited. The literature search revealed only one site where ISV has been applied for the remediation of lead, cadmium, or zinc in soil. At this site, ISV was applied for treatment of soils containing both organic (pesticides, dioxins) and inorganic (lead, mercury, and zinc) contaminants. As with *in situ* S/S, ISV is a commercially available technology, but it is offered by only a single vendor—GeoSafe, in Richmond, Washington (U.S. EPA 1997). ISV was demonstrated under the EPA's SITE program at the Parsons Chemical Superfund Site in Grand Ledge, Michigan (U.S. EPA 2000b; see Case Study #2).

3.1.2.3   Summary of Technology Status and Application

EPA reports that vitrification (presumably both *in situ* and *ex situ*) has been operated at a large scale at least 10 times, and has been demonstrated in more than 150 tests of varying scale on a broad range of soils and sludges (Engineering Bulletin 2000). However, as discussed above, only one site was identified where ISV was applied to metals-contaminated soils. In general, ISV is applicable for sites containing non-volatile metals at levels that do not exceed their glass solubilities (e.g., <25 wt%), or for high concentrations of organic contaminants (e.g., >10 wt%) (Engineering Bulletin 2000; Evanko and Dzombak 1997). The EPA reports that ISV may or may not be applicable for lead and cadmium. The effectiveness will depend on the difficulty associated with maintaining the metals within the melt, and the ability to control volatile emissions. The contaminated soils must also contain sufficient glass-forming materials (SiO_2 >30 wt%, Na + K >1.4 wt%) (Engineering Bulletin 2000).

ISV has been demonstrated to depths of 20 ft and is not considered to be cost effective at depths of less than 6 ft. The presence of buried metal or underground structures/utilities within 20 ft of the melt zone may preclude the use of ISV (Engineering Bulletin 2000). Finally, ISV may not be appropriate for soils with a slope of >5%, because the melted soils may flow (Engineering Bulletin 2000). Table 3 provides a summary of the advantages and disadvantages of ISV.

Table 3. Summary of the advantages and disadvantages of *in situ* vitrification for remediation of soils contaminated with lead, cadmium, and/or zinc

Advantages

Commercially available.

Results in an inert, impermeable product.

Demonstrated for lead and zinc.

Potentially effective over a wide concentration range.

Potentially effective for mixed contamination (e.g., inorganic and organic).

Disadvantages

Not cost effective for shallow contamination (<6 ft), and only demonstrated to a depth of 20 ft.

Requires control and treatment of volatiles.

Requires specific site conditions (e.g., slope <5%; sufficient SiO_2, Na, K; lack of subsurface interferences).

Requires capability for high energy input.

End land use may be compromised.

Expensive.

Case Study #2: *In situ* vitrification of pesticide-, dioxin-, and zinc-contaminated soils at the Parsons Chemical Site
Location: Grand Ledge, Michigan
Reference: U.S. EPA 1994, 2000a
Metal Contaminant: Zinc concentration of 150 mg/kg. Multiple additional contaminants present (including pesticides, dioxins, VOCs, SVOCs,[3] and heavy metals) also present. Contamination resulted from agricultural chemical manufacturing processes.
Area/Volume of Treated Area: Nine 26-ft × 26-ft squares, 16-ft deep melt cells. Total volume treated = 3,000 yd^3
Soil Properties: Silty clay with high moisture content; density 1.48 tons/yd^3
Problem Statement: Operations at a former agricultural chemicals mixing, manufacturing, and packaging facility resulted in soils containing a variety of organic and inorganic contaminants. In 1993–1994, a SITE demonstration program evaluated *in situ* vitrification as a means to treat the soils.
Action: *In situ* vitrification was applied to treat 3,000 yd^3 of contaminated soils. The process was completed in nine melt cells, with each melt requiring 10–19.5 days to complete.
Results: The treated (vitrified) soils met all treatment standards for TCLP leachable contaminants and off-gas emissions.
Outcome: *In situ* vitrification was found to be effective at treating the contaminated soils and achieving the treatment objectives. The treatment cost was $270/yd^3.

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[3] SVOC = semivolatile organic compound

3.2 Removal

For the purposes of this report, removal technologies are considered to be the well-established engineering approaches that are employed *in situ* to remove metals from a contaminated soil matrix through the use of physical and chemical processes. Two types of *in situ* removal technologies were identified—eletrokinetic remediation and soil flushing—and are discussed below.

3.2.1 Electrokinetic Remediation

3.2.1.1 Technology Description

Electrokinetic Remediation (ER) involves the installation of electrodes into the ground surface and application of low-intensity direct current through the soil to stimulate electrochemical and electrokinetic processes that desorb metals and polar organics from the soil matrix and mobilize them toward the electrodes for removal or treatment (FRTR 2001). Positively charged ions, such as lead, cadmium, and zinc, migrate toward the cathode, while negatively charged anions (such as arsenic) migrate toward the anode. The process results in the generation of an acid front at the anode and a base front at the cathode. The acid front eventually moves from the anode to the cathode, enhancing the desorption/dissolution of metal contaminants (U.S. EPA 1997). Ionic transport occurs by two primary mechanisms—electromigration and electro-osmosis. Electromigration is the transport of charged species under an electric gradient, while electro-osmosis is the transport of soil pore fluid under an electric current (U.S. EPA 1997). Electromigration is the dominant mechanism in operation with ER (FRTR 2001). Water or some other suitable solution may be added to enhance the mobility of contaminants and improve the performance of ER remediation systems.

ER can take the form of two approaches. The process can be applied to concentrate the contaminants at or near the electrode for subsequent removal and *ex situ* treatment. Removal can be achieved via excavation, electroplating at the electrode, precipitation at the electrode, pumping of water near the electrode, or complexing with ion exchange resins (FRTR 2001). Alternatively, ER can be used to induce the migration of contaminants through treatment zones (e.g., permeable reactive barrier) placed between the electrodes.

3.2.1.2 Summary of Literature Search Results

ER is a fairly well-developed technology and is offered in various forms by several vendors. Three notable reports were identified that describe ER technologies—the EPA's report, *Recent Developments for In Situ Treatment of Metal Contaminated Soils* (U.S. EPA 1997); and the Ground-water Remediation Technologies Analysis Center (GWRTAC) reports, *Remediation of Metals-Contaminated Soils and Groundwater* (Evanko and Dzomback 1997) and *Electrokinetics* (Cauwenberghe 1997). In addition, the literature search recovered several documents pertaining to ER remediation of soils contaminated with lead, cadmium, and/or zinc.

As part of the literature search, six sites were identified where electrokinetics has been evaluated on a pilot scale or implemented full scale in the U.S. and Europe for remediation of lead, cadmium, and/or zinc in soils (Table 4). At five of these sites, ER was reported to be effective at reducing the soil concentrations of lead, and at one of the sites, cadmium and zinc. However, much of the information obtained appears to have been vendor provided, and the available data are very limited. As a result, insufficient information was available to allow for a critical evaluation of the treatment performance and for presentation of a case study. The sixth site was a pilot study in Point Mugu, California, to evaluate ER removal of cadmium and chromium from a sandy soil (U.S. EPA 2000c). This study indicated that ER was ineffective under site conditions, despite the fact that preliminary laboratory bench-testing results had been favorable.

The effectiveness of ER technologies is a function of the contaminant concentration and type, and the soil type, structure, and chemistry; and it can be limited by the degree of solubilization and desorption of the metal contaminant that is achievable (Technology Overview Report 1997). ER is most applicable to saturated soils (although it can be effective for unsaturated soils) with low groundwater flow rates and moderate to low permeability (Evanko and Dzombak 1997). The use of ER is also limited in highly conductive soil matrices, because these matrices will have a higher energy demand to effect remediation.

Several bench-scale studies available in the literature have suggested that ER is a potentially effective means for the remediation of lead, cadmium, and zinc in contaminated soils. However, as highlighted by the experiences described above for the Point Mugu site, bench-scale tests represent idealized conditions and are not necessarily representative of ER performance at the field scale. Furthermore, many of the laboratory studies involve the use of soils that are "spiked" with a target metal. In general, the resulting mineralogic form in the spiked sample is likely to be present as a more readily available (e.g., soluble) mineral form than it may be in the soil at a given site.

Hamed et al. (1991) demonstrated 75–95% removal efficiencies in kaolinite soils spiked with lead. Wong et al. (1997) recorded similar removal efficiencies for lead and zinc in an artificially contaminated sand matrix. However, Reed et al. (1996) achieved only modest recoveries of lead during bench testing of an artificially contaminated silty loam. Clifford et al. (1993) demonstrated that ER can be fairly effective at removing high levels of spiked cadmium and zinc, and that the addition of EDTA and ammonia improved lead removal efficiency. However, the authors found that efficiency decreased at lower spike levels. Poor recovery of cadmium was reported from samples of artificially contaminated kaolinite, glacial till, and silty loam, due to precipitation of cadmium in higher-pH regions of the soil samples (Reddy and Parupudi 1997; Reddy and Chinthamreddy 1999). Mohamed (1996) evaluated the use of ER for removal of lead, cadmium, and zinc from a silty sand and a sandy silt, with the addition of sodium acetate, tap water, and distilled water as conditioning fluids. The author found that ER was effective for removal of cadmium, but only achieved moderate to poor removal efficiencies for zinc and lead, and concluded that removal efficiency depends on the initial concentrations of the contaminants, the mineralogy, the period of treatment, the strength of chemical reagents, various electrical parameters, and the experimental design.

Heterogeneities common to contaminated soil systems could limit the effectiveness of ER in field-scale applications. Marceau and Broquet (1999) demonstrated that the removal of

cadmium from a clay can be adversely affected by soil heterogeneity and can lead to portions of the soil horizon remaining untreated. Similarly, Yeung et al. (1996) found that the presence of impurities, such as iron oxides, can limit the effectiveness of ER removal of lead from kaolinite. Furthermore, in a pure sample, Yeung et al. (1996) found that 90% of the spiked lead became concentrated within 15% of the soil matrix adjacent to the cathode. This concentration effect was likely the result of the precipitation of lead as insoluble oxide and carbonate minerals within the high-pH zone induced in the soil adjacent to the cathode during the treatment process, and demonstrates the importance of electrode conditioning to ensure complete treatment.

In an EPA SITE program, Electrokinetics, Inc. performed a pilot-scale evaluation of ER for removal of lead from kaolinite soils and kalonite and sand mixtures spiked with lead nitrate. Electrodes were spaced at 70 cm (2.3 ft) within each sample (U.S. EPA 1995, 1997). ER processing resulted in a consolidation of more than 90% of the lead mass within the last 7 cm of the sample adjacent to the cathode.

Table 4. Summary of pilot- and full-scale applications of electrokinetic remediation

Site	Initial Concentration, (mg/kg)	Final Concentration (mg/kg)	Volume/Area Treated	Findings
Former Paint Factory, Europe	Pb >3,780 Cu >1,220	Pb <280 Cu < 200	8,100 ft^3 of peat/clay soil	Remediation reported to be successfully completed.
Military Air Base, Europe	Pb 730 Cd 660 Zn 2,600 Cr 7,300 Cu 770 Ni 860	Pb 108 Cd 47 Zn 289 Cr 755 Cu 98 Ni 80	68,000 ft^3 of clay soil	Remediation reported to be successfully completed.
U.S. Army Firing Range, Louisiana	Pb ≤4,500 TCLP Pb >300 mg/L	Pb <300 TCLP Pb <4 mg/L	Not provided	Pilot testing reported to be successful.
Operational Galvanizing Plant	Zn >1,400	Zn <600	1,350 ft^3 of clay soil	Remediation reported to be successfully completed.
Temporary Landfill	Cd >180	Cd <40	194,000 agrillaceous	Remediation reported to be successfully completed.
Point Mugu, California	Cd ≤1,810 Cr ≤25,100	Limited effect	Two 1/8-acre test cells treated to 10-ft depth. Sandy soil and sediment	Pilot-test treatment of a sandy soil. Poor performance was observed under field conditions. Inconsistent with findings of laboratory bench tests.

3.2.1.3 Summary of Technology Status and Applicability

Electrokinetic remediation is a commercially available technology offered in various forms by several vendors. The technology has been investigated recently in the United States, but has seen more widespread application in Europe. Additional research is required to achieve regulatory acceptance of ER as a viable technology in the United States. ER has potential applicability for lead, cadmium, and zinc over a wide range of concentrations. ER is most applicable to relatively shallow depths for the treatment of clays and other low- to moderate-permeability soils, under saturated or semi-saturated conditions. The effectiveness is sharply reduced at moisture contents of less than 10% (FRTR 2001). The presence of soil heterogeneities and subsurface anomalies can result in non-uniform and incomplete treatment. Furthermore, treatment of metal contaminants may require the use of conditioning fluids to ensure high removal efficiencies. An advantage of ER technology is that it does not substantially alter the soil physical properties and thus does not limit the potential site use.

Costs for ER are estimated to range from $20 to $225 per cubic yard (Technology Overview Report 1997). Table 5 summarizes the potential advantages and disadvantages of ER technologies.

Table 5. Summary of the advantages and disadvantages of electrokinetic remediation of soils contaminated with lead, cadmium, and/or zinc

Advantages
Commercially available.
Some studies suggest ER can be effective for remediation of lead, cadmium, and zinc. However, the data are somewhat limited and additional research is required.
Results in removal of the contaminant from the soil matrix.

Disadvantages
Efficiency limited by the solubility and desorption of the contaminant from the soil matrix.
Heterogeneity and subsurface anomalies can lead to incomplete treatment.
Electrode conditioning may be required to prevent metal precipitation near the electrode.
Secondary treatment/disposal may be required for metals removed from the soil matrix.
May not be effective for high-permeability soils, high-conductivity soils, or soils with very limited moisture.
The oxidation/reduction reactions induced by the ER process could lead to undesirable products (e.g., chlorine gas, trihalomethanes).

3.2.2 Soil Flushing

3.2.2.1 Technology Description

Soil flushing is an extension of soil washing technologies in which water or another suitable extraction solution is applied *in situ* to extract precipitated and adsorbed contaminants from the soil matrix. The extraction fluid is passed through the soil matrix via infiltration or injection techniques, and the extraction fluid is recovered. This fluid is then treated to remove the

contaminant, and if possible, the extraction fluid is recycled. When reagents are used, a key factor to efficient and cost-effective operation of soil flushing is re-use of the reagents.

3.2.2.2   Summary of Literature Search

The literature search found 18 documents pertaining to the use of soil flushing for the remediation of lead, cadmium, and zinc in soils. Soil flushing has been applied predominantly for the treatment of organic contaminants and has been applied for the treatment of metals at a limited number of sites. EPA reported in 1997 that soil flushing technologies have been selected as the preferred remedy for remediation of metals at seven Superfund sites, but was only operational at two of them (U.S. EPA 1997). The remaining sites were in the pre-design or design stage. One site, the Lipari Landfill in New Jersey, involves the extraction of leachate and injection to flush contaminants, including lead, from the landfill.

A fair amount of literature is available describing research related to soil flushing for removal of lead, cadmium, and zinc from soils. The majority of the research presented involves simple bench-scale testing of potential reagents that can be used to create an effective extraction fluid. In general, these tests represent idealized conditions and do not consider the difficulty of applying the technology under field conditions.

EDTA is the most commonly investigated reagent for enhancing removal of lead from soils, and several researchers have demonstrated its potential effectiveness (Price et al. 1998; Elliott and Herzig 1999; Doong et al. 1998). The EPA cites a laboratory study that evaluated the use of HCl, EDTA, and $CaCl_2$ to enhance the removal of lead from a coarse, sandy loam with a low organic content (U.S. EPA 1997). The study found that both HCl and EDTA were effective at extracting lead, and that the degree of removal achieved was a function of the pH decrease resulting from the reagents. The sensitivity to pH suggests that these reagents may not be effective in soils with significant acid-neutralizing capacity. Furthermore, the researchers concluded that use of the two reagents under field conditions at the rates applied during the laboratory study was not practical due to the cost of the reagents. It should also be noted that application of reagents such as HCl and EDTA can substantially alter the chemical properties of the soil and compromise its ability to support plant growth.

Similarly, Wasay et al. (1998) found that EDTA was highly effective at extracting not only lead, but also cadmium and zinc, but that the extraction efficiency was highly dependent on pH. On the other hand, Peters and Shem (1995) demonstrated that EDTA was a potentially effective extracting agent for lead, and that the removal efficiency was relatively insensitive to pH. The cause of the differing findings of these researchers is unknown, but may be related to the form in which the lead was present in the soil types tested.

Several other extraction fluids have been evaluated at the bench scale. Wasay et al. 1998 found that citrate, tartrate, a mixture of oxalate and citrate, and DPTA were highly effective at removing lead, cadmium, and zinc. Furthermore, these authors suggested that salts of weak organic acids were preferred over EDTA and DPTA, because they remove fewer macronutrients from the soils during treatment. Other organic compounds have been shown to be effective for lead extraction, including Tiron, d-glucconic acid, S-carboxymethyl-L-cysteine, and N-(2-acetamido)iminodiacetic acid (Price et al. 1998; Ting-Chien-Chen and Hong 1995).

Oxalate was found to form insoluble salts with lead and was thus ineffective in one bench study (Elliot and Herzig 1999). Citric acid demonstrated good recovery rates for lead, but only moderate recovery of zinc and poor recovery of cadmium (Francis and Dodge 1998). Ting-Chien-Chen and Hong (1995) used a numerical model to evaluate the potential effectiveness of more than 190 chelates for lead, cadmium, and zinc. The authors confirmed the model predictions for three selected chelates in bench studies—demonstrating good recovery of all three metals. Furthermore, the authors concluded that the metals and chelates have the potential to be recovered and recycled. Doong et al. (1998) demonstrated that anionic and cationic surfactants can enhance desorption of lead, cadmium, and zinc, but was only able to achieve moderate removal efficiencies. Brusseau et al. (1997) demonstrated that cyclodextrin enhanced cadmium removal (80–95%) from spiked sand, clay, and organic soil. Laboratory studies of a biosurfactant demonstrated moderate to poor recovery of zinc and cadmium, and poor recovery of lead (Mulligan et al. 1999a,b).

3.2.2.3 Summary of Technology Status and Application

Although the concept of soil flushing is well understood and widely accepted, it has seen limited application for metals-contaminated soils. This fact reflects the complexity of applying the technology under field conditions. In general, the metal removal efficiency during soil flushing depends on the degree of contact achieved between the extraction fluid and the contaminated soil matrix, and the solubility of the metal in the extraction fluid. As a result, soil flushing is most appropriate for contaminants that are highly soluble in the selected extraction fluid and that do not tend to sorb to the soil matrix as the metals-laden extraction fluid migrates to the water extraction point. Furthermore, there is considerable uncertainty in estimating the completeness with which the applied flushing reagents will be captured, and thus, a significant potential exists for spreading the contamination to underlying soils and groundwater resources. In addition, the chemical reagents can substantially alter the soil properties and limit the soils' ability to support plant growth.

Soil flushing is most appropriate for relatively homogeneous and permeable soils (i.e., $>10^{-5}$ cm/s). Heterogeneities can lead to channeling of extraction fluids and, thus, incomplete treatment. Soil flushing is not limited by depth, provided that recovery of the metals-laden extraction fluid can be ensured. Determination of an appropriate extraction fluid is likely to be the key factor to the use of a soil-flushing remedy for lead, cadmium, and zinc in soils. Based on the basic chemical properties of lead and cadmium in soils, the EPA speculated that soil flushing has the greatest potential to be applicable for lead in acidic sands, and for cadmium in permeable soils with low clay, low cation exchange capacity (CEC), and moderate acid content (Engineering Bulletin 2000). If an extraction fluid other than water is used, the ability to recover and reuse the extraction fluid is a major determinant of the overall cost. Lead, for example, is efficiently extracted under acidic conditions (e.g., through the use of weak acids or EDTA). However, neutralization of the extraction fluid by the soil matrix may inhibit the use of acidic extraction fluids at the field scale. Due to the complexity of identifying an appropriate extraction fluid, soil flushing is most appropriate for sites where removal of a single target metal is required.

The costs for soil flushing will vary among sites, depending on the efficiency of extraction achievable and the extraction fluid required. Estimates of cost range from $50 to $200/yd^3

(Evanko and Dzombak 1997). Table 6 summarizes the potential advantages and disadvantages of soil flushing technologies.

Table 6. Summary of the advantages and disadvantages of soil flushing for remediation of soils contaminated with lead, cadmium, and/or zinc

Advantages
Relatively simple to implement.
Removes the metal from the soil matrix.
Demonstrated for organic contaminants, but less well demonstrated for metals.
Not substantially limited by depth of contamination, although capture of extraction fluid is more complicated at greater depth.

Disadvantages
Appropriate extraction fluid must be identified and is highly site specific.
Potential for spreading contamination if recovery of the extraction fluid is incomplete.
Not effective for low-permeability and/or heterogeneous soils.
Can substantially compromise soil quality and affect the soil's ability to support vegetation.
Treatment of multiple contaminants in soils is complicated.
Potential exists for extracted metals to sorb to aquifer matrix before the extraction fluid can be recovered.

3.3 Stabilization

3.3.1 Technology Description

For the purposes of this report, stabilization technologies include those that involve the addition of chemical amendment(s) to reduce the leachability and/or bioavailability of lead, cadmium, and/or zinc in contaminated soils. Stabilization technologies are designed to render the metal contaminant inert (i.e., non-toxic or non-bioavailable) and/or immobile by inducing specific chemical and/or physical reactions. As shown in Figure 1, a metal can be rendered inert or immobilized in soils by several different processes. These processes include: a) non-reversible metal sorption in micropores/crystals or defects, b) metal diffusion into an added mineral, c) metal occlusion by other surfaces, d) metal precipitation, and e) occlusion of metals in stable organic matter (McLaughlin 2001).
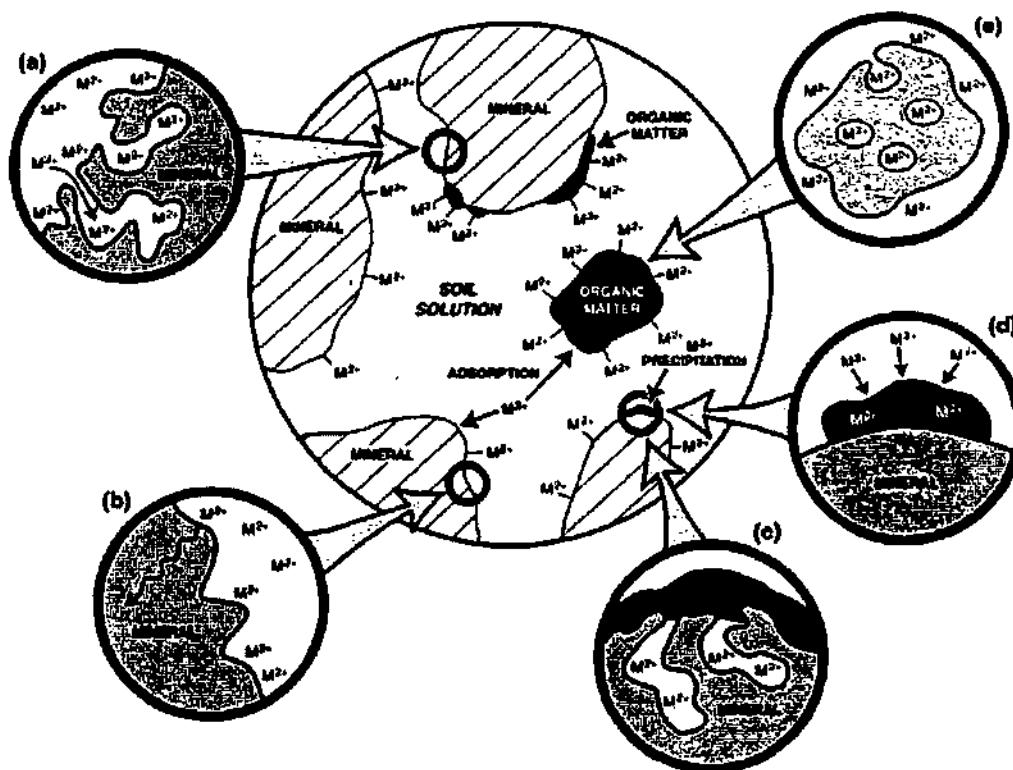
Figure 1. Schematic diagram of potential processes that can reduce metal bioavailability and mobility in soils in response to chemical amendment (McLaughlin 2001).

In concept, *in situ* application of stabilization technologies parallels *in situ* solidification/ stabilization (S/S) applications, and is thus subject to many of the same constraints. The primary distinction between stabilization and S/S technologies (for the purposes of this report) is that stabilization technologies involve the use of generally non-conventional chemical amendments to induce specific chemical reactions within the soil matrix. Unlike many S/S approaches, stabilization technologies do not target encapsulation of the metal contaminant or a reduction in the permeability of the treated soil matrix. Typically, lower amendment addition rates are use during stabilization remedies, relative to S/S remedies, and the problems associated with increased soil volumes following S/S treatment are not a significant issue for stabilization remedies. Stabilization remedies do not substantially alter the soil properties (e.g., permeability, volume, structure), so the end use for the site generally is not restricted, as can be the case with S/S technologies.

A substantial amount of research has been conducted to evaluate the potential efficacy of stabilization technologies for the remediation of lead, cadmium, and zinc in soils. The majority of these studies are bench-scale laboratory investigations—particularly evaluating the effects of phosphate amendments on lead solubility. However, several additional amendments have also been evaluated (e.g., zeolites, clays, beringite, lime, iron-based materials). A recent research focus has been on an integrated stabilization and phytoremediation strategy, termed "phytostabilization," which couples the use of specific soil amendments and plantings to remediate a site. These strategies are described in Section 3.4.

Several companies offer proprietary chemical formulations for the stabilization of metals in soils and, although several field applications of these amendments were found during the literature search, these studies have not been included in this report. Because these amendments are proprietary, it is often unclear by which mechanisms the amendments are operating to stabilize metals in the soils. Typically, reports on the use of proprietary amendments are provided by the vendor, lack sufficient detail for a critical evaluation, and do not provide a clear indication that the data have been subjected to rigorous peer review. Finally, reports on the use of proprietary technologies are almost always directed at reduction in soil metals mobility (typically based on TCLP or SPLP analysis), and very little testing is performed to evaluate the efficiency of the amendments at reaching other remedial end points (e.g., reduced bioavailability and plant uptake).

3.3.2   Summary of Literature Search

Numerous documents and case studies regarding the use of stabilization technologies for lead, cadmium, and zinc were identified during the literature search and selected for this literature review. Table 7 summarizes selected field applications of stabilization technologies.

3.3.2.1   Phosphate-Based Remediation

Phosphate-based amendments have the potential to be effective for lead, cadmium, and zinc (Phosphate Induced Metal Stabilization [PIMS] 2000). However, owing to its prevalence, high toxicity, and extremely low solubility in the presence of phosphate, lead has been the focus of the majority of the investigations (Lambert et al. 1997). In fact, Nriagu (1974) demonstrated nearly 30 years ago that phosphate addition reduced the amount of soluble lead in aqueous solutions. Several researchers have demonstrated the use of phosphate amendments to stabilize lead—most commonly through the use of natural and synthetic apatite minerals. The concept is to induce the formation of highly insoluble lead phosphate minerals that are known to be stable under a variety of environmental conditions. An added benefit is that the bioavailability of lead (both to humans and plants) may be greatly reduced when the lead is converted to phosphate mineral forms (Ruby et al. 1994)—a benefit that is likely not realized using standard cement-based S/S technologies.

Apatite and hydroxyapatite (calcium phosphates), in both natural and synthetic forms, are the most commonly investigated sources of phosphate for the remediation of lead, cadmium, and zinc in contaminated soils. Several investigators have demonstrated that apatite is highly effective at reducing soluble lead in soils and aqueous solutions (Boisson et al. 1999a,b; Chen et al. 1997; Rabinowitz 1993; Ma et al. 1993, 1995; Xenidis et al. 1999; Zhang et al. 1998). Furthermore, several of these researchers also reported favorable reductions in cadmium and zinc mobility (Boisson et al. 1999a,b; Chaney et al. 1997). In addition, *in vitro* testing and animal studies have indicated that apatite amendments are effective at reducing the bioaccessibility of lead in humans (Martin 2001; Mosby 2000). Apatite amendments have also been shown to be effective at reducing the uptake of lead, cadmium, and zinc by plants (Chlopecka and Adriano 1997; Laperche et al. 1997), and at reducing the phytotoxicity of metals-contaminated soils (Boisson et al. 1999a). Apatite was more effective than lime at reducing the phytoavailability of zinc in barley—particularly at high zinc concentrations

(Chlopecka and Adriano 1997). Zhang et al. (1998) reported that the formation of stable lead phosphate phases may depend on the soil pH. Dissolved phosphate resulting from apatite (and other sources of phosphate) amendment also has the potential to increase the mobility and plant uptake of arsenic (Boisson et al. 1999a; Boisson et al. 1999b). However, these effects can be offset by the inclusion of iron (e.g., as hydrous ferric oxide) with the phosphate amendment (Jones 1997; Martin 2001).

Several other forms of phosphate have been evaluated as potential amendments for stabilization of lead, cadmium, and zinc in soils. More soluble sources of phosphate, such as KH_2PO_4, NaH_2PO_4, and phosphoric acid, have been shown to be effective at sequestering these metals as phosphate minerals and reducing the bioaccessibility of lead (Berti and Cunningham 1997; Cotter-Howells and Capom 1996; Mosby 2000; Martin 2001), and according to Lambert et al. (2000), may in fact be somewhat more effective at sequestering lead than apatite. However, Kusuba et al. (1996) suggest that full-scale applications may require that they be used in conjunction with phosphate rock to provide a long-term source of phosphate to offset phosphorus removal from the soils by plants and microbes. Phosphate fertilizers, such as Triple Super Phosphate (TSP), are also potentially effective sources of phosphate for lead, cadmium, and zinc stabilization (Martin 2001). Other potential sources of phosphate identified by this literature search include peat, N-Viro soil, cattle manure, and poultry litter (Cotter-Howells and Capom 1996; Pierzynski and Schwab 1993; Martin 2001).

Thomas basic slags (TBS), a phosphate mineral that results from steel metallurgy wastes, were investigated as a potential chemical amendment on several contaminated soils (Vangronsveld and Cunningham 1998). In two sandy soils that had historically received applications of metal-rich sewage, TBS deceased the uptake of cadmium and zinc in ryegrass (Mench et al. 1994a,b). Furthermore, amendment with TBS allowed dwarf beans to grow on the soils, which would not support bean growth prior to amendment.

Laboratory studies of smelter-affected soils from Trail, British Columbia indicated that various sources of phosphate, including TSP, phosphoric acid, and apatite, were effective at reducing the bioaccessibility and leachability of lead (Martin 2001). Furthermore, combinations of phosphate and iron oxide were effective at reducing lead bioaccessibility while preventing an increase in the leachability of arsenic from the soils. However, pilot testing of the phosphate/iron oxide amendment failed to achieve a significant reduction in lead bioaccessibility. It is speculated that insufficient mixing was achieved to induce contact of the amendment, water, and the soil lead mineral phases to induce the lead phosphate mineral formation reaction.

The U.S. Department of Defense (DoD), under the Environmental Technology Certification Program, is conducting a field-scale demonstration of the use of a phosphate amendment to stabilize lead in soils at the Camp Stanley Storage Activity subinstallation of the Red River Army Depot in Boerne, Texas (Wright et al. 2002). This study is using crushed fish bone, known as Apatite II, as the source of phosphate. Apatite II is composed primarily of amorphous hydroxyapatite. A total of 3,000 yd^3 of soil has been treated effectively, based on the preliminary results. Although this treatment process was technically *ex situ* (the soils were

excavated, mixed *ex situ*, and placed back in the ground), the treatment process could also be applied *in situ*.

As described in Case Study #3, an EPA-sponsored field study at the Jasper County Superfund Site in Missouri evaluated the effects of phosphoric acid amendment and a mixture of TSP and iron oxides (as Iron-Rich^{TM} material [IRM], a byproduct of TiO_2 production) on lead bioavailability in soils affected by historical smelting and mining activities (Mosby 2000). The study indicated that phosphate amendments could effectively reduce lead bioavailability—potentially by as much as 69% in adult humans (Ryan and Berti 2001). Additional field studies at this site evaluated combinations of phosphate, iron, and compost amendments. This investigation demonstrated that all of the amendments were effective at reducing plant lead uptake, with the exception of an amendment consisting of 1% P and 2.5% Fe, which did not reduce plant uptake of lead. Selected soil treatments (1% P and 2.5% Fe, 1% P, and 10% compost) were subjected to *in vivo* testing for lead bioavailability in weanling rats and juvenile swine. Results indicated that the three amendments reduced lead by 38%, 28%, and 36%, respectively (Ryan and Berti 2001).

3.3.2.2   Non-Phosphate-Based Amendments

Several non-phosphorus-based amendments have been evaluated to stabilize lead, cadmium, and zinc in soils. The majority of these amendments operate by providing sorption sites that have a strong affinity for trace metals, thereby limiting the soluble fraction of the metal in the soil matrix. However, some of the amendments also induce an increase in soil pH, resulting in the formation of relatively insoluble oxides and carbonates.

Lime, a common soil amendment used in agriculture, is likely the oldest and most widely adopted immobilization amendment for cationic metals in soils. Lime addition induces a rise in soil pH, causing metals to precipitate as oxides and carbonates. Lime has been shown to be effective at reducing plant uptake of zinc and thus reducing zinc phytotoxicity (Krebs et al. 1998). Mixed results have been reported for plant uptake of cadmium in lime-amended soils (Krebs et al. 1998). The cadmium concentration is an important determinant in the effectiveness of lime amendments—at lower cadmium concentrations, factors other than pH can be important.

The influence of separate and combined limestone/manure applications on the availability of lead, zinc, and cadmium to soybeans in alluvial soils was evaluated (Pierzynski and Schwab 1993). Limestone was found to reduce the fraction of labile zinc in the soil, increase plant yields, and decrease metal concentrations in plant tissues. At the Palmerton Zinc Superfund site, lime, alone and in combination with high-iron, composted biosolid sludge, was tested for inactivation of zinc and cadmium (Li and Chaney 1998). Limestone alone was found to react very slowly in high-zinc-content soils, but was very effective when combined with the high-iron biosolids and applied as a phytostabilization strategy. Lime is anticipated to be effective only for a relatively short period of time before the pH-buffering capacity is depleted. As a result, repeated applications are often required (Vangronsveld and Cunningham 1998).

Addition of iron, in the forms of hydrous ferric oxides (HFO), steel shot, zero-valent iron, and IRM has been shown to be effective at reducing the leachability and bioaccessibility of metals (Berti and Cunningham 1997; Chlopecka and Adriano 1997Pierzynski and Schwab 1993; Shuman 1997). Manganese oxides (e.g., birnessite and hydrous manganese oxide [HMO]) have also been demonstrated to be effective at stabilizing metals in contaminated soils. Lab and pot experiments demonstrated that amendment with 1% HFO reduced the calcium nitrate-exchange and EDTA exchangeable fractions of cadmium and zinc in two contaminated soils, but generally did not reduce shoot uptake by ryegrass and tobacco (Didier et al. 1992; Sappin-Didier et al. 1997). Furthermore, HFO was not as effective as HMO in these studies. Steel shot is an attractive potential chemical amendment, because the shots readily corrode and oxidize, providing a continual, long-term supply of fresh HFO and HMO at the shot surface. Steel shot has been shown to be effective at reducing the mobility and phytoavailability of cadmium, zinc, and lead in several contaminated soils (Mench et al. 1994a; Didier et al. 1992; Gomez et al. 1997). The effectiveness of steel shot for stabilizing metals in soils increases with decreasing particle size and increased addition rates.

The French-German Cooperation Network on Soil Contaminated by Trace Elements evaluated the use of five iron-bearing materials (1% Fe) to stabilize cadmium and zinc in contaminated harbor mud (Gomez et al. 1997; Müller and Pluquet 1997). The iron materials included red mud from the aluminum industry, sludge from drinking water treatment, bog iron ore, native steel shot, and steel shot waste from descaling of untreated steel plate. All of the amendments caused a reduction in cadmium concentration in wheat grain, straw, spinach, and ryegrass. The red mud and water treatment sludge decreased the soluble fraction of cadmium and zinc in the soils by over 50%, while the other amendments were less effective. Soil treatments in the field trial were less effective than in pot tests for reduction of cadmium and zinc concentrations in plants and soil extracts. Chlopecka and Adriano (1997) found that IRM (5% Fe) amendments decreased the fraction of exchangeable zinc in a silt loam soil spiked with flue dust.

Birnessite and HMO were evaluated as chemical amendments for several French soils contaminated with metals (Mench et al. 1994a,b; Didier et al. 1992; Sappin-Didier et al. 1995). Both Mn-based amendments, particularly when combined with lime, were found to be effective at stabilizing cadmium and zinc, reducing the phytoavailability of the metals, and enhancing plant growth. However, the beneficial effects of birnessite did not persist beyond three harvests of ryegrass. HMO, which was developed through precipitation from potassium permanganate in an acidic medium, reduced cadmium in plant tissues regardless of soil type or plant species, but the phytoavailability of lead and nickel was reduced only in ryegrass. HMO has also been shown to be very effective for lead-contaminated sites, where the immobilization of lead was enhanced by combined application with lime (Mench et al. 1994a).

Aluminosilicates and natural and synthetic zeolites (crystalline, hydrated aluminosilicates) are another potentially effective amendment and have been demonstrated to have a high retention capacity for metals (Chlopecka and Adriano 1997; Edwards et al. 1999; Garcia-Sanchez et al. 1999). Al13 and Al-montmorillonite are potentially effective for cadmium and zinc, but may not be effective for lead (Lothenbach et al. 1997). Furthermore, Badora et al. (1998) found that these amendments may not be effective in soils with significant organic matter and may, in fact, increase the mobility of cadmium and zinc in such soil systems. Zeolites have been shown to be effective at reducing the plant uptake of lead, zinc, and cadmium from contaminated soils

(Chlopecka and Adriano 1997b; Gworek 1992; Rebedda and Lepp 1994; Miinyev et al. 1990). However, Didier et al. (1992) found that Al-pillared smectite, in combination with lime, was less effective than HMO, HFO, and steel shot at stabilizing metals in two metal-contaminated soils. Krebs-Hartmann (1997) found that montmorillonite, Al-montmorillonite, and gravel sludge resulted in a decrease in $NaNO_3$-extractable zinc and cadmium, accompanied by a reduction in zinc uptake, in red clover in a series of pot experiments. Gravel sludge was the only amendment that reduced cadmium uptake in test plants, potentially due to its acid-buffering capacity.

Boisson et al. (1999) demonstrated that amendment with beringite (a modified aluminosilicate that originates from fluidized bed burning of coal refuse), particularly when combined with steel shot, was effective at reducing the mobility of lead, cadmium, and zinc. Field and laboratory testing indicate that beringite is an effective amendment for reducing the bioavailability and mobility of lead, zinc, and cadmium, and that the effects of treatment are long lasting (Vangronsveld and Cunningham 1998). Beringite was shown to be effective at reducing lead, cadmium, and zinc uptake by garden vegetables in residential kitchen gardens affected by fallout from a zinc smelter in Lommel-Maatheid, Belgium (Vangronsveld 1998a; see Case Study #4).

As part of a joint study between the University of Washington and the Institute of Arable Crops Research, a laboratory investigation was conducted to assess the capability of various amendments (including lime, lime and TSP, water treatment residuals, water treatment residuals and biosolids, and red mud) to restore vegetative cover for zinc and lead mine tailings from Jasper County, Missouri (Brown et al. 2002, pers. comm.). In this study, the soils were treated with the chemical amendments and then seeded with rye grass. All of the amendments were found to enhance plant growth and to reduce the amount of water-extractable zinc.

Table 7. Summary field applications of stabilization technology at metals-contaminated sites

Site	Metals (mg/kg)	Amendment	Area/Volume Treated	Post-Treatment Results	Citation
Joplin County Superfund Site, Joplin, MO	Pb (1,000–5,000)	Phosphoric acid, TSP, rock phosphate, Compro®, IRM, compost	Various	Phosphate-based amendments were effective at reducing lead bioavailability based on *in vivo* and *in vitro* testing, and plant uptake studies.	Ryan and Berti 2001; Mosby 2000; Berti et al. 1998
Trail Lead Site, Trail, British Columbia	Pb (1,00–1,500) Cd (15–30)	Phosphate rock combined with iron fillings, two proprietary amendments	Three 10-x10-ft plots, treated to a depth of 6 in.	Field testing could not replicate laboratory bench tests, and limited reduction in bioavailability observed in field-treated samples. Speculated that insufficient mixing was achieved.	Martin 2001
Palmerton Zinc Superfund Site, Palmerton, PA	Zn (12,650) Cd (880)	Limestone	Not provided	Lime was applied and soil plots planted with one metal-tolerant and three non-metal-tolerant turfgrass species. Lime was not effective at establishing permanent vegetation, but it alleviated some of the phytotoxicty and may have reduced the potential for metals leaching.	Li and Chaney 1998
Lommel-Maatheid Kitchen Soils, Belgium	Zn (92–980) Cd (3.1–9.4) Pd (170–682)	Beringite	10 residential garden plots, dimensions not provided	Application of beringite amendment substantially reduced uptake of metals by garden vegetables. Laboratory column tests indicate that the effects of the beringite amendment are likely to persist well into the future.	Vangronsveld 1998b
INRA Couhins experimental farm, Bordeaux, France	Cd (3.9–122) Ni (12.4–269	Beringite	Not provided	Application of the beringite amendment reduced Ca-nitrate extractable cadmium and nickel and decreased the mobility of these metals. No phytotoxicity symptoms were evident, and the cadmium and nickel content in maize leaves grown in the treated soils was generally reduced.	Boisson and Mench 1998

3.3.3 Summary of Technology Status

The literature search revealed that a broad variety of amendments have the potential to be effective at fixing lead, zinc, and cadmium in soils—thereby reducing the mobility and bioavailability of these metals. Phosphate-based amendments have received the most attention and appear to be the most promising for lead. However, the majority of the studies to date have been on a laboratory scale, and these approaches are not fully demonstrated under field conditions. As a result, uncertainty remains regarding the ability to achieve uniform and stable treatment of metals in soil under field conditions.

Research in this area has paid close attention to the potential for the amendments to reduce the bioavailability of lead in the soils to humans and thus to reduce its toxicity. Although several parallel research efforts have been undertaken to develop reliable and repeatable means of determining lead bioavailability in untreated and treated soils, additional research is required before such measures are fully acceptable to regulatory agencies and the public (see Section 1.3). Furthermore, although observed reductions in lead bioavailability resulting from phosphate amendments have been significant (i.e., on the order of 30–60%), depending on the target remediation objective, it may not be feasible to achieve sufficient reductions to render heavily contaminated soils safe to be left in place. In general, research involving zinc- and/or cadmium-contaminated soils has focused on the ability of the amendment to reduce the mobility, plant uptake, and phytotoxicity of these metals in soils. Although substantial research indicates that chemical amendments can be highly effective at achieving these endpoints, the lack of mechanistic understanding for these effects has hampered their widespread application.

As with *in situ* solidification/stabilization, *in situ* stabilization requires uniform mixing of the chemical amendments throughout the contaminated matrix. In general, the same types of approaches used to mix reagents and soils for *in situ* S/S can be used for *in situ* stabilization. It is worth noting, however, that many vendors of *in situ* S/S technology have proprietary mixing systems that are not readily available for use in stabilization applications. The ability to achieve complete mixing is likely the primary physical hurdle to successful application of stabilization approaches for remediation of lead-, cadmium-, and zinc-contaminated soils.

Due to the relatively developmental status of stabilization technologies for *in situ* remediation of lead, cadmium, and zinc in soils, costs for implementing these technologies are uncertain. However, given the similarity of stabilization technology to S/S technology (Section 3.1.1), it is reasonable to consider that the two technologies would be of similar cost. As discussed in Section 3.1.1.3, S/S technologies can cost $20–$40/yd^3 to as much as $100–200/yd^3 depending on the depth of treatment. However, the majority of stabilization-based remediation applications are likely to be for surficial soils that represent a direct contact exposure risk. Furthermore, stabilization technologies typically require far smaller application rates than S/S technologies. As a result, it is anticipated that the majority of the stabilization applications would fall at or below the lower-end cost estimate of $20–40/yd^3.

Table 8 summarizes the potential advantages and disadvantages of stabilization technologies.

Table 8. Summary of the advantages and disadvantages of stabilization for remediation of soils contaminated with lead, cadmium, and/or zinc

Advantages

Has the potential to effectively reduce both the mobility and bioavailability of metals.

(Non-proprietary) amendments are generally readily available and inexpensive.

Can be applied over a wide range of depths.

Application generally relies on simple, inexpensive technologies that are well established.

Disadvantages

Effectiveness of chemical amendments has not been adequately demonstrated, and the concept of reducing metal bioavailability (particularly to humans) has not been embraced by the regulatory community.

Contaminant remains in place, raising concerns about the long-term stability under field conditions.

Uniform mixing may be difficult to achieve, and site-specific conditions (e.g., cohesive soils, oily sands) may preclude application.

Arsenic, and potentially other metals, has the potential to be mobilized by addition of phosphate-based amendments. However, inclusion of additional amendments (e.g., HFO) can minimize or prevent arsenic mobilization.

Exerts some limitations on the future land use of the remediated soils.

Case Study #3: Stabilization of lead in soils

Location: Joplin, Missouri

Reference: Mosby 2000; Berti et al. 1998; Brown et al. 2002; Ryan and Berti 2001

Metal Contaminant: Lead derived from smelter stack fallout (1,000–5,000 mg/kg)

Area/Volume of Treated Area: Various

Soil Properties: Silt loam soil, pH 6.9–7.2, organic matter 4.6%

Problem Statement: Lead and zinc mining and smelting activities since the mid 1800s have resulted in widespread lead contamination in local soils. Stabilization technology is being considered as a simple, inexpensive, and relatively non-disruptive remediation alternative for treatment of the soils.

Action: In the Mosby (2000) study, phosphoric acid at amendment rates of 5,000 and 10,000 mg-P/kg was applied to various test plots by rototilling, pressure injections, and surface application. The chemical amendments TSP, rock phosphate, Compro®, and IRM in various combinations and amendment rates were also evaluated in other test plots. The test plots were sampled at various times following amendment and analyzed for lead bioavailability (via *in vitro* testing, animal [swine and rat] soil dosing, and human dosing) and lead leachability.

The Brown et al. (2002) study was conducted in a similar manner and evaluated the following amendment formulations: phosphorus (as TSP and rock phosphate), iron (as IRM) and phosphorus (as TSP), compost, and compost and phosphorus (as TSP). The amendments were applied to test plots using a rototiller. The plots were neutralized with lime and seeded with tall fescue. The plots were sampled four months later and evaluated for plant lead uptake, *in vitro* lead bioaccessibility, and *in vivo* lead bioavailability (rat and swine dosing).

Results: In the Mosby (2000) study, phosphoric acid was generally found to be the most effective of the phosphate-based amendments evaluated. The study demonstrated that phosphoric acid amendment (0.5% and 1% P w/w) reduced lead adsorption in young swine by an average of ~35%. In addition, preliminary data from the soil amended with 1% P indicated a 69% reduction in lead bioavailability when dosed to adult humans (Ryan and Berti 2001). Phosphoric acid was also shown to reduce lead uptake by fescue planted on the test plots, but did not significantly influence cadmium and zinc uptake.

Case Study #3 (continued):

Results (continued): In the Brown et al. (2002) study, all of the amendments tested resulted in a decrease in lead bioaccessibility, with the reductions being most pronounced in the samples containing the greatest amount of phosphate added as TSP. In general, a similar trend was observed in reductions in plant uptake of lead. Addition of iron as IRM to the TSP amendment did not substantially affect the amendment performance and may, in fact, have reduced the TSP amendment efficiency. Amendment with 10% compost was found to reduce lead bioaccessibility and plant uptake, although to a somewhat lesser extent than TSP at 3.2% P. *In vivo* testing of soils amended with compost (10%) and IRM (2.5% Fe) indicated reductions in lead bioavailability of 36% and 38%, respectively.

Outcome: The results of the Joplin studies demonstrate that stabilization is a potentially viable technique for reducing risks associated with lead-contaminated soils by reducing the fraction of lead that is bioavailable. Stabilization strategies offer a low-cost and simple alternative to excavation and disposal of lead-contaminated soils.

Case Study #4: Zinc- and cadmium- contaminated kitchen gardens
Location: Lommel-Maatheid, Belgium
Reference: Vangronsveld 1998b
Metal Contaminant: Zinc (9.2–980 mg/kg) and cadmium (3.1–107 mg/kg) in kitchen garden soils affected by fallout from a local zinc smelter.
Area/Volume of Treated Area: Residential gardens. Size not provided.
Soil Properties: Not provided
Problem Statement: Soils in residential vegetable gardens in Lommel-Maatheid have elevated metals concentrations resulting from fallout from a former zinc smelter. Vegetables grown in these gardens are known to accumulate these metals within edible tissue, thus creating a pathway for human exposure.
Action: Field tests were conducted on 10 gardens to evaluate the efficiency of beringite amendments to reduce plant uptake of metals. A total of 5% (w/w) of beringite was rototilled to a depth of 25 cm into the soils. Laboratory column tests were conducted using the amended soils to simulate rainfall percolation through the soils over a 30-year period to evaluate the long-term effectiveness of the beringite amendment at immobilizing cadmium and zinc.
Results: The beringite amendment was found to reduce the uptake of cadmium and zinc in plants grown in the treated garden soils (relative to those grown in untreated garden soils). In the first year, a 2–4 times reduction in cadmium concentration was observed in the edible tissue of garden vegetables. Over time, the metal uptake continued to decrease. By the second year, cadmium concentrations in the high cadmium-accumulating species (spinach, celery, lettuce) were below the guideline value of 0.2 mg/kg (wet wt) in all but one of the gardens tested. Zinc and cadmium uptake in lettuce grown in the treated plots gradually decreased to levels consistent with control plants grown in non-metal-containing soils. The laboratory column tests demonstrated that beringite addition dramatically reduced the mass of cadmium and zinc flushed from the contaminated soils and that these effects are likely to persist well into the future.
Outcome: The results of the field trial indicate that beringite amendment offers a means of reducing plant uptake of cadmium and zinc in garden soils. This simple and inexpensive treatment approach reduces cadmium and zinc mobility and uptake in plants, and these effects are likely to be long lasting.

3.4 Phytoremediation

Phytoremediation, described as a natural process carried out by plants, especially those that have been able to survive in contaminated soil and water, is considered a potentially cost-effective remedial solution for many sites, in the U.S. and abroad, that have organic and inorganic contaminants (Salt et al. 1998). The following two primary techniques have been developed for the phytoremediation of metals-contaminated soils:

- Phytoextraction: By successive croppings of plants that tolerate and accumulate heavy metals, the metal contaminants can be translocated from soil to shoot tissues. This allows metals to be removed from the soil through the harvest, and the plant tissue can be smelted to recover and recycle the soil metals (Brown et al. 1994a,b).

- Phytostabilization: A combination of plants and soil amendments are applied to metal-contaminated soils to reduce the risk posed by the soil by decreasing the metal bioavailability and mobility (Vangronsveld and Cunningham 1998).

The growth of interest in the phytoremediation field is driven by its relative cost efficiency compared to standard remediation methods for government-mandated site cleanup (Watanabe 1997).

3.4.1 Phytoextraction

Two general approaches have been developed for phytoextraction of metals—continuous phytoextraction and induced phytoextraction. Continuous phytoextraction involves the successive cropping of plants that can accumulate high levels of metals (hyperaccumulators) to extract metals from contaminated soils over a period of time. Induced phytoextraction involves the use of metal-chelating agents or other amendments to increase the solubility of metals in soils and to enhance extraction efficiency by plants that grow quickly and generate a large amount of biomass. Both approaches represent potential means for remediation of lead, cadmium, and zinc in shallow soils.

3.4.1.1 Summary of Literature Search

The potential cost benefits of phytoremediation for metals-contaminated soils has stimulated a large amount of recent research—the majority of which focuses on identification of potential hyperaccumulating species, and evaluation of the use of chelates and high-biomass crops for induced phytroextraction approaches. Successful full-scale applications of phytoremediaton for metals-contaminated soils are still rare; however, a number of pilot-scale investigations have been conducted.

Laboratory Studies — A considerable amount of research has been devoted to identifying and comparing plant species that have the potential to hyperaccumulate metals such as zinc, cadmium, and lead. The ideal plant for continuous phytoextraction should grow on metal-bearing soil, exhibit high biomass and growth rates, accumulate and resist high concentrations

of metal in shoots, have the ability to accumulate several metals, and exhibit resistance to diseases and pests (Salt et al. 1998; Watanabe 1997). Metal hyperaccumulators have been defined as plants that can tolerate more than 1,000 m/g of cobalt, copper, chromium, lead, or nickel, or 10,000 mg/g of manganese or zinc in the dry matter (Baker and Brooks 1989). The first hyperaccumulators characterized were members of the Brassicacaea and Fabaceae families, and according to Salt et al. (1998), at least 45 plant families are known to contain metal-accumulating species.

The effect of soil metal concentration on metal uptake is not fully understood. Dudka et al. (1996) found that zinc and cadmium uptake by a variety of crop plants was best described with a plateau (saturation) model. Davis et al. 1995 found that cadmium concentrations in crop plants increased with increasing rates of metal-rich flue dust addition to the soils. Salt et al. (1995a,b) established that as cadmium concentrations in a hydroponic nutrient solution exceeded 0.6 μg/mL, the accumulation rate of cadmium in Indian mustard (*Brassica juncea*) shoot and xylem sap increased dramatically. Blaylock et al. (1997) studied the uptake of lead in *B. juncea* and explained that high total lead concentration in the soil does not necessarily result in high lead concentrations in aboveground plant shoots, due to lead's relative insolubility, and although *B. juncea* has the potential to accumulate lead and cadmium, this species cannot efficiently remove these metals from the soil matrix unless the metals are solubilized. However, Xiong (1997) showed that the lead level in soil was positively correlated with lead accumulated in *Sonchus oleraceus* plant tissues, and Dudka et al. (1996) explained that the relation between lead in soils and plants was indeed linear. In the presence of a chelating agent such as EDTA, lead concentrations in soil solution appear to be associated directly with lead accumulation in plants (Huang et al. 1997). Furthermore, according to McLaughlin (2002, pers. comm.), *B. juncea* does not really have a genetic potential to accumulate metals; it can only accumulate metals at a significant rate once damage to the roots occurs with EDTA addition.

Synthetic metal chelates that enhance the water solubility of metal complexes by combining with metals in solution have been shown to enhance or induce heavy metal accumulation in a variety of plant species. High-biomass crop plants such as Indian mustard (*B. juncea*), corn (*Zea mays*), and sunflower (*Helianthus annuus*) have been shown to accumulate high concentrations of lead when chelates such as EDTA were applied to the soil medium (Blaylock et al. 1997; Huang et al. 1997). Through their studies, Blaylock et al. (1997) reported that the addition of synthetic chelators, specifically EDTA, to lead- and cadmium-contaminated soil greatly enhanced uptake in *B. juncea*, possibly by first acting to complex the soluble metals in soil solution, so that as free-metal activity decreases, dissolution of bound metal ions begins to compensate for the shift in equilibrium. Elless and Blaylock (2000) found that the EDTA-extractable lead in eight lead-contaminated soils corresponds primarily to the exchangeable and carbonate fractions of each soil, and that lead associated with organic, oxide, and residual fractions was solubilized relatively inefficiently by EDTA. A high concentrations of EDTA or very low pH is required to solubilize these lead forms. Ebbs and Kochian (1998) reported that barley consistently accumulated more zinc than *B. juncea*, but determined that, in contrast to the effect of chelates on *B. juncea*, barley and oats do not respond to addition of EDTA. Blaylock et al. (1997) showed that acidification of soil in conjunction with EDTA additions resulted in further increases in lead accumulation. Huang et al. (1997) also examined five different chelating agents on pea and corn lead uptake. These authors reported that the effectiveness decreased in the following manner: EDTA > HEDTA > DTPA > EGTA > EDDHA.

According to Huang et al. (1997), environmental concerns regarding the bioavailability of heavy metals in potential forage will dictate that chelate additions be minimized. They suggested that chelates should be added to root zones when the vegetation is well-established on lead-contaminated sites, so that plants can be harvested shortly thereafter (lead accumulation in plant shoots is rapid). In this manner, the plants would contain relatively low lead concentrations for most of their life span, thereby limiting the time that wildlife may be exposed to the lead due to consumption of the lead-rich plant tissue.

Soil acidity plays a strong role in dictating uptake of heavy metals in plants (Chlopecka and Adriano 1997; Brown et al. 1994a, b). The influence of soil pH on the availability of metals depends on the geochemical properties of the metal as well as on several other variables (Li and Chaney 1998). For example, phytoavailability of zinc can be decreased by adding organic matter to soil, causing formation of insoluble zinc organic complexes with humic acids, thereby lessening the risk of zinc toxicity to plants (Li and Chaney 1998). Limestone applications can raise soil pH, thereby reducing plant concentrations of heavy metals, and metal phytotoxicity (Davis et al. 1995; Li and Chaney 1998). In contrast, Li et al. (1996) studied the effects of limestone treatments on cadmium uptake in sunflowers (*Helianthus annuus*), but the limestone application did not reduce cadmium uptake and transfer to sunflower kernels. They suggested that the deep roots of the sunflower exceeded the depth of the limestone application, nullifying the effect of the limestone on cadmium uptake. Brown et al. (1995) suggested that, during phytoextraction, the number of croppings necessary to remove metals may be decreased if soil pH is lowered, thereby increasing metal solubility. Brown et al. (1995) demonstrated in the field that decreasing the soil pH increased the uptake of zinc and cadmium by the hyperaccumulator *Thlaspi caerulescens*.

Some plants are able to produce metal-binding polypeptides, known as phytochelatins (PCs), to sequester metals and render them unavailable for transport within the plant (Ross and Kaye 1994; Salt et al. 1998). Phytochelatins function by complexing with heavy metals in the plant and thus detoxifying them. High levels of PCs have been found in plants that display tolerance to heavy metals. *Brassica juncea* has been shown to produce phytochelatin/cadmium sulfide complexes that may contribute to higher metal tolerance through more effective sequestration of cadmium (Speiser et al. 1992). Although a variety of metals, including lead, cadmium, and zinc, induce phytochelatin synthesis in plants, studies of lead and zinc detoxification in plants seem to indicate that mechanisms other than phytochelatins are also involved. For example, the precipitation of zinc as zinc-phytate represents a zinc detoxification mechanism, and the precipitation of lead as carbonates, sulfates, and phosphates also plays a role in the detoxification of this metal in plant tissues (Salt et al. 1998). Davies et al. (1991, as cited in Vazquez et al. 1992) suggested that phytochelatins do not play a role in zinc tolerance in *Festuca rubra* roots, due to the presence of buthionine sulfoximine, a phytochelatin inhibitor.

Summary of Field Applications and Pilot Studies — Blaylock and co-workers, in 1997, conducted a study to evaluate the efficacy of induced phytoextraction of a contaminated soil containing 1,200 mg/kg of lead. The study evaluated uptake by Indian mustard (*B. juncea*) using EDTA and a combination of EDTA and acetic acid to induce lead solubilization. The field study demonstrated that lead uptake was greatly enhanced by the addition of the chelating agents. The authors estimated that the approach would be capable of removing 180 kg of lead per hectare in a single growing season.

A field demonstration, funded by the Environmental Security Technology Certification Program, was conducted to evaluate the efficacy of phytoextraction to remove lead from soils at the Twin Cities Army Ammunition Plant in Minneapolis-St. Paul, Minnesota (U.S. EPA 2000d; USAEC 2000). The demonstration involved the application of EDTA in concert with acetic acid (to lower soil pH) to corn crops, then subsequently to white mustard crops. Low corn yields and lead concentrations observed during the testing were attributed to the poor agronomic quality of the soil. Lead concentrations in harvested white mustard were also very low, possibly due to limited rooting patterns and/or the fact that lead had moved downward into the soil below the root zone, due to residual EDTA left after the corn harvest. The researchers suggested that alternative mustard varieties be used in the future, and that fertilizers be applied to encourage greater biomass. Additionally, deep tilling should be used to return lead that may have seeped downward in the soil profile closer to the surface, and perhaps a more efficient irrigation system for EDTA should be used.

Brown et al. (1995) evaluated cadmium and zinc uptake by *Thlaspi caerulescens*, silene, and lettuce in two-year-long field studies of soils contaminated by historical sewage sludge applications. The tests evaluated uptake at soil pH levels of ~5 and 6.5–7. The researchers found that zinc was hyperaccumulated by *Thlaspi caerulescens*, but that cadmium was accumulated at rates similar to those of the other plants. The authors conclude that phytoremediation is a potentially feasible approach for metal-contaminated soils, but is most likely limited to less contaminated soils. Furthermore, nutrient addition and pH adjustment likely will be required, and remediation is likely to take a fair amount of time. The authors estimate an 18-growing-season treatment period for a soil containing 400 mg/kg zinc.

Edenspace Systems Corporation (formally Phytotech, Inc.) is a leading firm in the commercial application of phytoremediation for metals-contaminated soils. Edenspace has conducted more than 19 phytoremediation projects since 1994—some of which are summarized in Table 9. Edenspace's work at the Magic Marker site in Trenton, New Jersey, is summarized in Case Study #6 below. However, it should be noted that the majority of the data presented herein are vendor provided, and have not been subjected to rigorous review. Some researchers contend that there is insufficient evidence collected in these investigations to conclusively support phytoextraction as the primary mechanism for reduced metals concentrations in the soils. It has been argued that the reduced concentrations are more likely the result of metal migration to greater soil depths in response to solubilization and downward migration with the chelate amendment.

Edenspace conducted a full-scale phytoremediation project to evaluate the reduction of lead concentrations and leachability in affected soils in Connecticut (see Case Study #5). Indian mustard and sunflower were investigated in various treatment plots. Two unspecified chemical additives were applied to the soils to increase lead availability. The results indicate a lead removal rate of 150–160 mg/kg per year, suggesting that a significant treatment period (5–10 years) will be required to achieve cleanup goals. The project reportedly achieved its goals in terms of reducing total lead concentrations and SPLP-extractable lead.

Edenspace has also completed a demonstration project at the U.S. Army's Fort Dix. This project established that sequential cropping of Indian mustard, sunflower, and a mix of rye and barley, in conjunction with soil amendments, reduced lead from 516 mg/kg to 290 mg/kg. Results of this study, however, demonstrated that solubilizing amendments can cause the downward migration of lead, and care must be taken to minimize the leaching of lead. Edenspace also reports field trials where phytoremediation was effective for lead in soils at a site near Boston, Massachusetts, and for removal of cadmium and zinc from soils at a Superfund site in Findlay, Ohio.

3.4.2   Phytostabilization

Phytostabilization-based remediation strategies involve the use of plants, solely or in conjunction with soil amendments, to stabilize a metal-contaminated soil by limiting metal mobility and bioavailability. Under ideal circumstances, phytostabilization would involve the use of metal-tolerant plants that immobilize/inactivate metals in soils through sorption, precipitation, complexation, or chemical reduction reactions (U.S. EPA 1997). Alternatively, high-water-yield plants, such as poplar trees, can also be used to lower the groundwater table locally and limit contact of shallow contaminated soils with groundwater. It should be noted that some researchers consider phytostabilization to be a containment technology that is most applicable as an interim measure (U.S. EPA 1997).

The most promising phytostabilization practice is to combine the use of plants and soil amendments to remediate metal-contaminated soils. The amendments act to reduce the bioavailability and phytoavailability of the metals in the soil, and/or restore a vegetative cover on the soils (Brown et al. 2002). This strategy was derived from revegetation efforts for the reclamation of mine spoils and smelter-affected soils, in which chemical amendments are often required to establish plant growth (Vangronsveld and Cunningham 1998). Chemical amendments may include those described in Section 3.2 to convert soil metals to a more geochemically stable state, such that the metals are less mobile and/or bioavailable. Often, an organic-based soil amendment is used, such as biosolids compost, to assist in revegetation efforts and, in some cases, to stabilize soil metals. Revegetation provides protection against erosion, reduces exposure to the metal-contaminated soils, and reduces infiltration of water and, thus, leaching of metals from the soils. Unlike phytoextraction, under a phytostabilization strategy, plants ideally would not accumulate metals in the aboveground plant tissue, which could be consumed by human or ecological receptors (Vangronsveld and Cunningham 1998).

3.4.2.1   Summary of Literature Search

The majority of the information derived from the literature search pertaining to the evaluation of phytostabilization for metal-contaminated soils consisted of descriptions of field trials rather than laboratory studies. This likely reflects the fact that phytostabilization strategies are typically geared toward sites with widespread metals contamination, such as mine wastes and soils containing smelter-stack fallout. Also, field studies are generally more appropriate for evaluation of revegetation, because large-scale environmental factors (e.g., climate) can be evaluated.

Phytostabilization has been studied by Lepp (1998) at the Prescot Copper Rod Plant, in Prescot, Merseyside, England. At this site, long-term field trials involving the use of two synthetic zeolites were conducted to stabilize metal-contaminated grasslands. Slurried zeolites were applied to plots of the grasslands (i.e., plant species were already established), and the plots were sampled after 12 months. The study demonstrated that the zeolite treatment substantially reduced the water-extractable metals concentrations in the soils, and the treated plots demonstrated greater growth.

Pierzynki et al. (2000) evaluated the ability of poplar trees to remediate lead and zinc contamination in soils affected by smelting activities in Kansas. A field study was conducted to evaluate the potential for the trees to phytostabilize the metals in place by minimizing the net percolation of water through the soils. The researchers found that the tree survival rate was poor—possibly due to poor field conditions (i.e., environmental conditions and poor agronomic practices) and/or zinc toxicity.

Brown et al. (2002) evaluated the effects of biosolids applications to reduce the bioavailability of lead in contaminated urban soils. In this laboratory study, samples of lead-contaminated soils were amended with various biosolids and incubated for 30 days. The lead bioaccessibility of the soils was then evaluated via an *in vivo* (weanling rat) study and various *in vitro* measures. This testing demonstrated that three of the biosolids resulted in lead bioavailability reductions of greater than 20% relative to the untreated soils.

Phytostabilization has been evaluated as a potential remedial strategy at the Palmerton Zinc Superfund site in Palmerton, Pennsylvania (Li and Chaney 1998). The soils in the area have been affected by former zinc smelting operations; the soils contain elevated cadmium and zinc concentrations and are often acidic. The phytotoxic nature of the soils has limited plant growth in the area, and the soils are subject to wind and water erosion. In field investigations, a high-iron, high-phosphorus biosolids compost combined with lime was evaluated as a potential soil amendment. .The compost was selected not only to improve the soil's ability to support vegetative growth, but also to provide iron and phosphorus to bind metals in soils—thereby limiting the mobility and bioavailability of the metals. The amended soils were then seeded with metal-tolerant and non-metal-tolerant turfgrasses, to minimize erosion of the amended soils and to reduce infiltration of meteoric water. The field demonstration found that the compost application decreased zinc and cadmium phytotoxicity and that all of the turfgrasses (including the three non-metal-tolerant species) exhibited excellent growth in the treated plots.

Biosolids have also been evaluated in field trials of phytostabilization for metals-contaminated mine tailings at various sites, including the Bunker Hill Superfund site, Idaho (Brown et al. 2002), a site in Leadville, Colorado (Compton et al. 2002), and a site in northern Idaho (DeVoder et al. 2002, pers. comm.). At the Bunker Hill site, Brown et al. (2002) evaluated surface applications of municipal biosolids in combination with other manufacturing residuals (wood debris, wood ash, pulp and paper sludge, and compost). The authors concluded that high-nitrogen biosolids, combined with a high-CEC residual (such as wood ash), are effective for establishing a healthy vegetative cover on mine tailings for a minimum of 3 years.

Biosolids were evaluated as a means to restore an ecosystem along a river drainage affected by mine tailings in Leadville (Compton et al. 2002). During this evaluation, large areas of affected

soils were treated with lime, biosolids, and a combination of lime and biosolids. The study demonstrated that the amendments were capable of restoring plant growth and a functioning ecosystem based on a number of biological indicators (e.g., increased organism diversity and populations), and reducing $Ca(NO_3)_2$-extractable zinc. However, lead, zinc, and cadmium levels were found to be elevated in the aboveground plant tissue.

Phytostabilization through the use of biosolids was evaluated in a greenhouse study at the West Page Swamp tailings repository in northern Idaho (DeVoder et al. 2002, pers. comm.) as a means to stabilize tailings in sediments. Unlike other phytostabilization applications, this study evaluated biosolids amendments in a saturated system, with the goal of creating highly reduced conditions such that low-bioavailability sulfide minerals (specifically, lead sulfide) would be formed. Three amendment formulations were evaluated: biosolids compost and wood ash; biosolids compost, wood ash, and low-level sulfate addition; and biosolids compost, wood ash, and high-level sulfate addition. The sediments were mixed with the amendments and planted with arrowhead and cattails. The study found that the biosolids and wood ash amendments alleviated the phytotoxicity of the sediments, and vigorous plant growth was established, with plant tissue metal concentrations remaining below levels of concern to wildlife. No plant growth occurred in the soils treated with amendments including sulfate. All of the amendments were found to reduce the ratio of simultaneously extracted metals to acid-volatile sulfide metals (SEM:AVS) within the amended sediments, indicating a decrease in the fraction of metals that are bioavailable to aquatic organisms. Furthermore, the amendments including sulfate reduced the SEM:AVS ratio in the sediments underlying the amended zone. The sulfate-based amendments were also more effective at reducing lead bioavailability based on *in vitro* testing.

Table 9. Summary of selected field demonstrations or full-scale studies of *in situ* phytoremediation

Site	Phytoremediation Description	Plant Type	Area/Volume Treated	Initial Metal Concentration (mg/kg)	Results
Twin Cities Army Ammunition Plant, Arden Hills, MN	Induced phytoextraction. Successive crops of corn and white mustard were grown. The soils were amended with EDTA and acetic acid.	White mustard, corn	8,100 ft^2	Pb 2,610	Performance objectives were not achieved. Poor Pb uptake and weather conditions. Lead and EDTA detected in the underlying shallow aquifer.
Magic Marker Site, Trenton, NJ (Edenspace)	Induced phytoextraction. Three crops of *B. juncea* harvested. Soils amended with EDTA.	*Brassica juncea*	4,800 ft^2 87 yd^3	Pb 200–1,800 Pb$_{ave}$ = 479	Treatment reduced the area exceeding the regulatory standard of 400 mg/kg for lead from 40% to 28%. Project was considered to be a success.
Industrial Facility, CT (Edenspace)	Induced phytoextraction and phytostabilization. Phytoextraction involving the use of two unspecified amendments to increase lead solubility. Phytostabilization was reportedly performed to reduce SPLP leachable soil lead levels, but details of these actions were not provided.	*Brassica juncea*; sunflower	1.5 acres Upper 45 cm of soil. 3,572 yd3	Pb >1,000	The project achieved its goals: reductions of lead concentrations (details not provided) and SPLP leachable lead. The final average SPLP extractable lead concentration was 0.097 mg/L (the treatment objective was 0.15 mg/L).
Residential Site, Dorchester, MA	Phytoextraction. Three successive croppings. Very few details provided.	Not available	1,081 ft^2	Pb 600–1,900 Pb$_{ave}$ = 1,200	Eliminated the area of soil with lead >800 mg/kg, which had originally accounted for 68% of the area.
Abandoned zinc and lead smelter site; Dearing, KS	Phytostabilization. Use of Poplar trees to immobilize metals in place, by reducing erosion and evapotranspiration of water.	Poplar trees	Not available	Pb and Zn concentration data not available	Tree survival rate was poor. Poor survival speculated to be due to the late planting date and adverse weather conditions, poor quality of initial trees, and/or the high zinc concentrations of the soils.

Site	Phytoremediation Description	Plant Type	Area/Volume Treated	Initial Metal Concentration (mg/kg)	Results
Beltsville, MD	Phytoextraction: Evaluated plant metal uptake in crops grown on sludge-amended soils.	*Thlaspi caerulescens; Silene vulgaris*	Study conducted on 126-ft^2 and 546-ft^2 plots	Zn 48.2–181.3 Cd 0.33–5.46	Concluded that phytoremediation is feasible. Cd uptake was affected by pH. Estimated 18 growing seasons would be required to remediate the soil.
Open Burn and Detonating Area, Ensign-Bickford Company, Simsbury, CT	Induced phytoextraction (see Case Study #5)	*Brassica juncea;* sunflower. Unspecified amendment added to increase Pb uptake.	0.35 acres	Pb 125–5,000	Decreased Pb concentrations from an average of 635 to 478 mg/kg, with the greatest removal occurring where Pb concentrations were the highest.
	Phytostabilization (see Case Study #5)	*Brassica juncea;* sunflower. Unspecified amendment added to increase Pb uptake and stabilize existing SPLP-leachable Pb.	2 acres	Pb 6.5–7.5	Resulted in an average reduction of 0.95 mg/L in SPLP-leachable Pb.

Case Study #5: Phytoextraction and phytostabilization of lead-contaminated soils at the open burn and open detonating area, Ensign-Bickford Company

Location: Simsbury, Connecticut

References: Edenspace 2002, U.S. EPA 2000e

Metal Contaminant: Lead in soils at an open burn and open detonating area. Lead concentrations of 125–5,000 mg/kg in the area treated by phytoextraction, and 6.5–7.5 mg/kg in the area treated by phytostabilization.

Area/Volume of Treated Area: Area treated by phytoextraction = 0.35 acres. Area treated by phytostabilization = 2.0 acres.

Soil Properties: Silt loam soils (pH 6.5–7.5)

Problem Statement: The soils at the Simsbury Connecticut site contained elevated concentrations of lead over a 2.35-acre area. Based on an XRF survey, four subareas totaling 0.35 acres were identified to contain the most highly elevated lead concentrations (typically >1,000 mg/kg). A fifth area had substantially lower lead concentrations.

Action: A phytoextraction-based remediation program was initiated to remove lead from soils containing greater than 1,000 mg/kg lead (areas 1–4). This program involved planting and harvesting of Indian mustard and sunflower plants. In addition, two chemical amendments were applied to the soils during the remediation program: an unspecified chemical additive designed to increase the phytoavailability of lead, and a site-specific foliar amendment to enhance lead removal from the soils and lead uptake and translocation into harvestable aboveground plant tissue. Three crops were planted: one of Indian mustard, one of sunflower, and one that was a mixture of Indian mustard and sunflower. A phytostabilization-based remediation program was initiated for soils that contained less than 1,000 mg/kg and greater than 0.015 mg/L of SPLP-leachable lead (area 5). A chemical amendment(s) was added to the soils to enhance plant biomass production and soil lead uptake, and stabilize SPLP-leachable lead.

Results: The phytoextraction program resulted in a decrease in the average soil lead concentration in areas 1–4, from 635 mg/kg to 478 mg/kg. The greatest reductions occurred in the soils that originally contained the highest concentrations of lead. It is estimated that continued application of the phytostabilization program would result in a reduction of 150–160 mg/kg per year in the site-wide average total lead concentrations. The phytostabilization program reduced the SPLP-leachable lead by 0.95 mg/L, such that the final average leachable lead (0.097 mg/L) was below the treatment objective of 0.15 mg/L.

Outcome: Edenspace reports that the combined phytoextraction and phytostabilization program was completed in 2000 and achieved its goals of reducing total lead concentrations and SPLP-leachable lead. The total cost of the combined phytoextraction/phytostabilization program was estimated to be $40/yd^3 of treated soil.

Case Study #6: Phytostabilization of metal-contaminated soils at a smelter site

Location: Lommel-Maatheid, Belgium

Reference: Vangronsveld (1998a)

Metal Contaminant: Soil contaminated with zinc (1,000–10,000 mg/kg), cadmium (8–61 mg/kg), and copper (80–1,400 mg/kg) due to smelter impacts

Area/Volume of Treated Area: 7.5 acres

Soil Properties: Acidic sandy soil, pH 4.5–5.9

Problem Statement: Former smelting activities at the Lommel-Maatheid smelter in Belgium have resulted in contamination of local soils—resulting in maximum zinc concentrations of greater than 20,000 mg/kg. A field demonstration project was conducted on a 7.5 acre plot of soils to evaluate the efficacy of phytostabilization to stabilize the metal-contaminated soils.

Action: During this study, the metal-contaminated soils were amended with beringite and compost, and then planted with the metal-tolerant species *Agrostis capillaries* and *Festuca rubra.*

Results: A healthy vegetative cover was established over the treated soil plots. After 5 years, the plots still showed no signs of phytotoxicity, and had an alkaline pH and increased organic matter and CEC relative to the untreated soils. In addition, the water-exchangeable fraction of zinc was up to 70 times lower in the treated soils. Furthermore, the treated plots demonstrated a greater richness of plant species relative to untreated soils, including the emergence of non-metal-tolerant species. These findings and observations of biological indicators (e.g., fungi, bacteria, nematodes) are evidence that a functional ecosystem is becoming established in the treated areas.

Outcome: The field study demonstrated that phytostabilization is a potentially effective technology for remediation of metal-contaminated soils.

3.4.3 Summary of Technology Status

The use of phytoremediation for the *in situ* remediation of soils contaminated with lead, cadmium, and zinc is still in the developmental stages. Nonetheless, phytoremediation remains a promising alternative for treatment of shallow soil contamination. Several field applications have indicated that induced phytoextraction can be effective for remediation of lead in soils, and may be effective for cadmium and zinc. However, the majority of the field demonstrations have involved relatively low concentrations of lead. Treatment of more heavily contaminated soils remains undemonstrated at the field scale and is likely to require long treatment periods (e.g., 5–10 years). Furthermore, there remains substantial concern regarding the viability of induced phytoextraction-based technologies. Some researchers contend that none of the field demonstrations have unequivocally demonstrated through metal mass balance calculations that the observed reductions in soil metals concentrations during induced phytoremediation are the result of plant uptake, as opposed to seepage of metal-EDTA complexes below the depth sampled (McLaughlin 2002, pers. comm.).

No full-scale applications of continuous phytoextraction were discovered during this literature search. However, continuous phytoextraction is still promising and may be preferred to induced phytoextraction, due to the potential for chelating agents to spread contamination to lower depths, and concerns about exposure to metals accumulated in the plants used during induced phytoextraction.

Phytostabilization is a promising remediation strategy for metals in soils—particularly for sites with widespread surface contamination where other remedies are impracticable. However, many regulators consider phytostabilization to be an interim technology for stabilizing metal-contaminated soils until such time that a final remedy can be implemented. Additional research is required to determine optimal amendment and planting conditions for a variety of site conditions. However, these conditions will vary from site to site depending on the nature of the site and the soil conditions.

Costs associated with induced phytoextraction are uncertain due to its developmental status, and will be highly site specific, depending on the concentration to be treated and the quantity of chelating agent required (if any). Despite this uncertainty, costs for phytoextraction are likely to be substantially less than conventional excavation and disposal, particularly for soils with low to moderate levels of contamination. Edenspace reported a cost of $40/yd^3 for induced phytoextraction treatment of low-level lead contaminated soils at the Simsbury, Connecticut site. The costs for phytostabilization-based remediation will depend largely on the amount and type of chemical amendments added. Costs can be extremely low if waste residuals (e.g., biosolids) from a local source can be used as soil amendments. Costs for a single application of biosolids-based amendments at the Leadville, Colorado, Palmerton, Pennsylvania, and Jasper County, Missouri sites were on the order of only $0.02–0.50/yd^2 (Brown 2002, pers. comm.). In many cases, however, it is probable that chemical amendments will be required to facilitate stabilization of the soil metals. In these cases, it is probable that costs would be on the order of $20–40/yd^3.

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Table 10 provides a summary of the advantages and disadvantages of the use of phytoremediation for treatment of lead, cadmium, and zinc in soils.

Table 10. Summary of the advantages and disadvantages of phytoremediation for soils contaminated with lead, cadmium, and/or zinc

Advantages

Removes metals from the soils.

"Green" technology.

Metals potentially can be recycled from harvested plant biomass.

Low cost.

There are some data that suggest induced phytoextraction is potentially effective on a field scale. However, these data are limited, and subject to debate.

Disadvantages

Only effective for shallow contamination.

Heavily contaminated soils may require long treatment periods.

Harvested plants require treatment and/or disposal.

Potential for downward migration of metals if chelating agent is used.

4   Summary

The critical review presented in this report describes the status of *in situ* remediation technologies for soils contaminated with lead, zinc, and cadmium. This report is intended to be a resource to the environmental community to assist in the evaluation *in situ* remediation technologies. Table 11 presents a summary of the findings of the critical review and the factors that will affect selection of an *in situ* remediation technology for soils containing lead, zinc, and cadmium. These findings are summarized under three general categories: technology status, typical remediation targets, and site-specific factors. These categories are defined as follows:

- *Technology Status*

    - Developmental status: The degree to which the technology is accepted by the environmental industry as a proven technology that has been developed for remediation of metal contaminated soils. Key aspects to be considered are the extent to which the mechanisms by which the technology operates are understood, and the extent to which it has been demonstrated at the field scale.

    - Regulatory acceptance: The extent to which the technology is accepted by the regulatory community as a means of achieving a remediation target that is protective of human health and the environment.

    - Cost: An estimate of the unit cost of each technology. In general, the costs for application of *in situ* remediation technologies, particularly the most innovative technologies, are poorly developed. Furthermore, many of the cost estimates are provided by vendors or researchers and may not be subject to critical review.

- *Typical Remediation Targets*—The extent to which the technology is capable of achieving the remediation targets of reducing metal mobility or bioavailability, or provide for revegetation of the metal-contaminated soil.

- *Site-Specific Factors*—Any potential limitations the technology may have for common, site-specific factors that frequently limit treatment effectiveness (such as site end use, metal concentration, soil properties, and depth and areal extent of contamination).

In a general sense, the majority of *in situ* remediation technologies for metals in soils are in the developmental stage and further research and site-specific testing are required prior to implementation at a given site. However, in many cases the costs associated with these additional efforts are warranted by the potential advantages offered by *in situ* remediation alternatives over conventional approaches.

Table 11. Summary of the review of _in situ_ remediation technologies for soils contaminated with lead, zinc, and cadmium

Remedial Strategy/ Technology	Technology Status		
	Development Status	Regulatory Acceptance	Cost[a]
Isolation			
Solidification/ Stabilization (S/S)	Well demonstrated and understood	Generally accepted means to reduce migration if tested for site conditions. May not be acceptable if bioavailability of metal is of concern.	Ranges from $20 - $200/yd³ depending on depth of treatment.
in situ Vitrification (ISV)	Demonstrated, but typically for organic or mixed contamination.	Likely to be accepted by the regulatory community.	Costs of $270/yd³ or more.
Removal			
Electrokinetic Remediation	Applied to several sites in Europe, but few in the US. Additional research is required.	Likely to be accepted by the regulatory community if demonstrated to be successful.	Ranges from $20-$225/yd³.
Soil Flushing	Insufficiently developed. Few applications under field conditions.	May be viewed unfavorably due to potential to mobilize metals and low development status.	Ranges from $50-$200/yd³.
Stabilization	Several studies indicate technology is effective. Additional research required.	Additional research required to gain acceptance of the strategy of reducing metal bioavailability, and of procedures to quantify that reduction.	Poorly developed, but likely similar to low end of S/S technologies ($20-$40/yd³).
Phytoremediation			
Phytoextraction	Demonstrated at some sites although there are concerns regarding the validity of the demonstrations. Additional research is required.	Has gained some regulatory acceptance, although concerns over technology effectiveness may hamper universal acceptance.	Poorly developed. One estimate of $40/yd³.
Phytostabilization	Some demonstration data available. Additional research is required.	Often considered an interim technology. Additional research required to demonstrate technology effectiveness.	Poorly developed, but potentially low (e.g., $20-40/yd³).

Table 11. Continued

Remedial Strategy/ Technology	Typical Remediation Targets		
	Reduce Mobility	Reduce Bioavailability	Provide for Revegetation
Isolation			
Solidification/ Stabilization (S/S)	Typical objective of this technology, and demonstrated to be effective in many cases.	Infrequently evaluated. Effectiveness typically unknown.	Soil properties may be compromised and may not support plant growth.
in situ Vitrification (ISV)	Typical objective of this technology and has been demonstrated in the field.	Although not typically quantified, likely to be effective.	Treated materials will not support vegetation
Removal			
Electrokinetic Remediation	Effective at reducing bulk metal mobility if sufficient removal is achieved.	May be effective at reducing bioavailability through removal of the soluble fraction of the metal, but has not been evaluated.	Treated soils are likely to support revegetation.
Soil Flushing	Effective at reducing bulk metal mobility if sufficient removal is achieved. Some potential to enhance mobility if flushing solution is not adequately captured.	May be effective at reducing bioavailability through removal of the soluble fraction of the metal, but has not been evaluated.	Treated soils are likely to support revegetation.
Stabilization	Demonstrated to be potentially effective.	Demonstrated to be potentially effective.	Treated soils are likely to support revegetation.
Phytoremediation			
Phytoextraction	Effective at reducing bulk metal mobility if sufficient removal is achieved. Potential to enhance metals mobility if due to application of chelating agent(s).	May be effective at reducing bioavailability through removal of the soluble fraction of the metal, but has not been evaluated.	Treated soils are likely to support revegetation.
Phytostabilization	Demonstrated to be potentially effective.	Demonstrated to be potentially effective.	Treated soils support vegetation.

Table 11. Continued

Remedial Strategy/ Technology	Site-Specific Factors				
	Site End Use	Pb, Cd, Zn Concentration	Soil Properties	Depth of Contamination	Areal Extent of Contamination
Isolation					
Solidification/ Stabilization (S/S)	Alters soil properties and volume. Site may not support vegetation and may require institutional controls to prevent human and ecological exposure.	Applicable to a wide range of concentrations.	May be precluded where large rocks, cohesive soils, oily sands and clays are present.	Can be applied up to 150 ft bgs.	Cost prohibitive to apply to large sites.
in situ Vitrification (ISV)	Alters soil properties and ability to support plant growth.	Applicable to a wide range of concentrations.	Effective for a broad range of soils.	Can be applied at depth, but would be costly at great depth. May not be effective for shallow soils.	Cost prohibitive to apply to large sites.
Removal					
Electrokinetic Remediation	Unlikely to substantially influence the end use for the site.	Likely applicable to a wide range of concentrations.	Most effective for clays and other low-K soils. Not likely to be effective in heterogeneous systems.	Most applicable to shallow metals contamination; not cost-effective for surficial soils contamination.	Cost prohibitive to apply to large sites.
Soil Flushing	May significantly alter soil properties and inhibit the soil's ability to support plant growth.	Most appropriate for low- to mid-level contamination. Highly contaminated soils are likely to require excessive flushing reagent.	Most applicable to relatively homogeneous, highly permeable soils.	Generally not limited by depth of contamination, although recovery of extraction fluid may be complicated with depth.	Cost prohibitive to apply to large sites.
Stabilization	Unlikely to significantly alter the site end use, although institutional controls may be required to minimize exposure.	Most appropriate for low to moderate levels of contamination.	Applicability may be limited by highly cohesive soils (e.g., clays) in which amendment mixing is difficult.	Likely can be applied up to 150 ft bgs. Most typically considered for treatment of surface soils.	May be a reasonable cost alternative for large contaminated sites.
Phytoremediation					
Phytoextraction	Unlikely to limit the final end use for the site.	Likely only appropriate for mildly contaminated soils where metals are phytoavailable or chelate-extractable. Heavily contaminated soils would require excessive treatment periods.	Only effective for soils that can support plant growth (potentially with nutrient or amendment addition).	Only applicable to surface contamination.	Potentially cost effective for sites with large areas of surface contamination.
Phytostabilization	End site use limited to vegetated state.	Most appropriate for low to moderate levels of contamination.	Only effective for soils that can support plant growth (potentially with nutrient or amendment addition).	Only applicable to surface contamination.	Potentially cost effective for sites with large areas of surface contamination.

* As a comparison, costs for excavation and offsite disposal of metal-contaminated soils can typically range from $200/yd^3 to more than $500/yd^3, depending on the volume of contaminated soil, the transport distance to a disposal facility, and whether the soils require stabilization prior to disposal.

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